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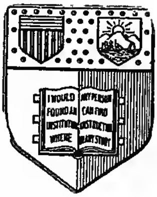

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VOL. XVII. FEBRUARY, 1922. PART 2.

PHYSICO-CHEMICAL PROBLEMS RELATING TO THE SOIL.

A GENERAL DISCUSSION.

At the meeting of The Faraday Society held on Tuesday, May 31, 1921, in the Rooms of the Chemical Society, Burlington House, London, a GENERAL DISCUSSION took place on "PHYSICO-CHEMICAL PROBLEMS RELATING TO THE SOIL". The meeting consisted of two sessions, from 4.30 to 6.30 and from 8 to 10.30 p.m.

Throughout the proceedings the Chair was occupied by **Sir A. Daniel Hall, K.C.B., F.R.S.** Alfred Daniel Hall

Professor Alfred W. Porter, President of the Society, introduced Sir Daniel Hall into the Chair with the following remarks.

SECTION I.—INTRODUCTION AND GENERAL PAPERS.

Professor Alfred W. Porter, D.Sc., F.R.S.: The main business this evening is to discuss the physico-chemical properties of soils. It has been inaugurated by the Faraday Society, but we have secured, to some extent at any rate, the co-operation by invitation of several other societies interested in the subject under discussion, *e.g.* the Biochemical Society, British Ecological Society, Association of Economic Biologists, and the Agricultural Educational Association. This is, I believe, the twenty-ninth General Discussion that has been organised by the Faraday Society, and in accordance with a custom which has often been followed in connection with these discussions, we have secured as Chairman some prominent man especially interested in the subject. To-day we have been fortunate in

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securing as Chairman Sir Daniel Hall, and I will now ask him to take the Chair.

Sir A. Daniel Hall, K.C.B., F.R.S.: The subject which we have to occupy ourselves with this afternoon and this evening is to review all the physico-chemical relationships of the soil. In that connection, of course, it is our business in particular to try to get together and summarise in the course of the discussion the changed aspect that the soil problems now wear in consequence of the development of the colloid hypothesis. I well remember, looking back to the time when I was first working on these problems, 25 or 30 years ago, when we were without the light that we now have, I began to try to account for some of the characteristic clay properties by a hypothesis built up solely upon the fineness of the particles composing the clay, without any regard to their nature. We very soon had to abandon that point of view. It was, indeed, untenable even at that time, but there was nothing very satisfactory to put in its place, and I think we shall learn in the course of this discussion how very changed are our views of many of the relationships, for instance, of soil to water, and all those problems of the physical behaviour of the soil—especially the nature of that dominant body that we call clay—and how they can be reduced to a reasonably simple working hypothesis. Without more ado, I will call on Dr. E. J. Russell to give us a general survey of the subject.

THE PHYSICO-CHEMICAL PROBLEMS RELATING TO THE SOIL—A GENERAL SURVEY.

BY E. J. RUSSELL, F.R.S., DIRECTOR OF THE ROTHAMSTED EXPERIMENTAL STATION.

Introduction.

From the earliest times soil investigators have realised that soil fertility involved both chemical and physical problems. Wallerius in the eighteenth century, Davy and Schübler in the early nineteenth and Liebig in the middle of the nineteenth century, all clearly recognised this. Later on there arose a tendency to specialisation, and soil physics began to develop as a subject apart from soil chemistry; but of recent years the borderland has been explored, and it is evident that the soil investigator can be helped considerably by the physical chemist, and conversely that physical chemistry will find interesting applications in soil work.

For our purpose we must look upon the soil as a complex system comprising four parts: (1) mineral particles; being disintegrated and decomposed rock fragments which, through the action of weather, water, ice and other factors, have in course of time been reduced to dimensions varying from about 1 mm. in diameter to molecular orders of magnitude. (2) Intermingled in most intimate fashion with all this is the organic matter, residues of past generations of plants and animals, which represents the source of energy for the large population of soil organisms. (3) The soil solution, being the soil water and everything dissolved therein.

These three are sufficiently obvious on mere inspection: the fourth is a matter of experiment and inference rather than of simple observation: soil possesses definite colloidal properties and therefore is assumed to possess a certain proportion of its substance in the colloidal state. Two hypotheses have been put forward: one, the older, to the effect that the colloidal properties are due to the fine particles known to be present; the other, and more recent, that they are due to a jelly surrounding each of the particles but having a proportionately greater effect on the finer than on the coarser ones because of the difference in extent of surface. It is possible that both cases arise in nature. The difference between the two views is less than might at first appear, because the finest particles may be regarded as being distributed over the surface of the larger ones and so forming a kind of discontinuous colloidal coating.

The mineral particles of the soil are derived from rocks, and some of their constituents occur in all soils, *e.g.* silica, certain silicates, etc. Further, the soils under any given set of climatic conditions have been subjected to these conditions for a very great period of time, and might be expected to have attained such degree of uniformity as climatic factors can impose. It is of course true that the geological forces which produced the particles have never ceased to operate and they still continue to act, but it is also true that somewhere in the history of the soil particles great differences have arisen which no subsequent events have ever blotted out. Thus, the Lias and Trias soils are entirely different, although they adjoin and are in many places under similar climatic conditions. And so it happens that there are certain definite soil types which the investigator recognises by the vegetation, and which the chemist and the physicist are gradually beginning to characterise. Three general classes can be recognised: a soil may be formed from disintegrated rock, as in the Paleozoic soils of North Wales or the granite soil of Aberdeen; or, there may have been considerable decomposition; in our climatic conditions the tendency is for silica to accumulate and for the bases including iron and aluminium oxides to become reduced in quantity; in certain sub-tropical countries, however, the silica disappears and the iron and aluminium oxides accumulate, giving the so-called laterite soils. I have no personal knowledge of laterite soils and shall not discuss them: the other two classes, however, do occur in this country. The soils consisting of disintegrated rock material are under investigation at Bangor by G. W. Robinson, and at Aberdeen by J. Hendrick and J. Orr; while the soils studied at Rothamsted consist of decomposed rock material. So far no fundamental difference seems to have emerged in physico-chemical properties, though it is possible that there may be a difference in the colloidal matter, the disintegration soils may owe their colloidal properties to fine particles while the decomposition soils possess the jelly.

Investigations have not yet proceeded sufficiently far to enable us to say much about the jelly. A good deal of work, however, has been done on the fine particles: these can be separated from soil by simple mechanical washing. No less than 20 per cent. of the soil at Rothamsted consists of particles having a mean diameter smaller than 0·002 mm., ranging downwards to ultra-microscopic dimensions; this fraction is called "clay". The name is too old to change but it is unfortunate. The word clay is already used in several senses: when Dr. Mellor speaks of clay he means something entirely distinct from the soil investigators' clay. Formerly there was no means of ascertaining whether or not the range of diameter was continuous, but Dr. Sven Odén, whom we welcome here to-day, has devised an elegant method by which a mass distribution curve can for the first time be obtained, thus giving the necessary information.

The clay particles possess the properties of an electro-negative colloid: their suspensions can be flocculated by addition of electrolytes; they show plasticity (though again the word is used in a sense different to that of Dr. Mellor); shrinkage; and in the mass clay can act as a semi-permeable material. The clay particles show some differences from silt, which will be described by Mr. Comber.

From the agricultural point of view the chief property of clay is its effect on the cultivation operations. A large amount (18 per cent. or over) of clay as defined above renders the soil difficult to work or "heavy"; a very small amount (4 per cent. or under) is usually associated with so low a water-retaining power that the soil becomes too liable to drought and of too loose a nature to allow of satisfactory plant growth. Between these limits lie most of the fertile arable soils of this country. With excess of clay some unsatisfactory features set in: water is retained too strongly; the resistance to implements becomes very great; and there is a marked impermeability to air and water.

Addition of calcium carbonate modifies these properties reducing their intensiveness and making a soil of 18 per cent. of clay behave as if it contained only 12 per cent. or 14 per cent. On one of our fields at

Rothamsted the draw-bar pull on the tractor during cross ploughing with a three furrow plough was 1500 lb. on the untreated soil, but 200 lb. less on the chalked soil. Calcium carbonate therefore in some way neutralises the special clay properties. How exactly this happens is not known. Some work has been done on flocculation, but little in this country on the other properties.

Probably the most difficult problems associated with clay are those connected with tilth. Every grower knows what is meant by tilth, yet no one could give a precise definition: it can, however, be described as the capacity of the soil to assume the nice crumbly condition suitable to a seed bed. Tilth is obtained by a series of processes: first ploughing, then harrowing, then rolling to break down large lumps, then letting them dry, then allowing them to become wet by rain, then again harrowing to break them down when at the right degree of wetness. It is, however, essential to have the previous drying; by no artifice can a good tilth be obtained in persistent wet weather. Precise information is lacking, but it appears that clay containing say 30 per cent. of water may exist in two states: one if it began at 40 per cent. and dried down to 30 per cent.; the other if it began at 20 per cent. and was moistened up to 30 per cent. In the former case cultivation results in sticky or "poached" masses, drying to hard steely lumps; in the latter it produces a good tilth. Parallel cases could no doubt be found among the colloids.

There are other curious effects of drying which are not yet easily explicable: an enhancement of fertility, increased rate of nitrification, etc.

Some of the organic matter of the soil, and particularly the part known as humus, is sticky and jelly-like, with power of absorbing certain soluble substances. Van Bemellen directed attention to the typical colloidal properties of humus, and Baumann has developed this view. Dr. Sven Odén and Mr. Page will go into this question more fully; it is sufficient here to point out that organic matter exerts so great an effect that 15 per cent. or 20 per cent. obliterates the sharp distinctions between sandy soil and clay soil, and gives a new type—humus soil—having special properties of its own. In colloidal properties humus differs from clay: thus it exerts a protective effect on the flocculation of clay.

Probably most of the important physico-chemical problems of the soil relate to the soil moisture or the soil solution. The water comes initially from the rain, but owing to the slowness of percolation and evaporation some is always left over between one shower and another, and this dissolves soluble material from the soil. It would of course ultimately become a saturated solution if the conditions were static, but they are always changing and so the solution varies both in concentration and in composition. Its agricultural importance, first emphasised by Whitney and Cameron, lies in the fact that it constitutes the immediate source of plant food: it is this which enters the plant root and helps in plant growth. There is a relationship between the concentration of the soil solution and the rate of growth of the plant, though apparently not the sharp proportionality that might at first be expected. Closer examination, however, shows that proportionality would be improbable; the solution is not imbibed as a whole, and the plant needs very considerably more of the water than it does of the dissolved plant nutrients. Thus, a good crop of wheat with its accompanying straw weighs about 4 tons per acre, and transpires during its lifetime about 1000 tons of water, *i.e.* 2·2 million lb. At the end of its life it contains only about 60 lb. nitrogen, *i.e.* $\frac{1}{36,000}$ of the water absorbed—an amount which would be introduced by a 0·0022 per cent. of nitric-nitrogen: actually the concentration in the soil solution is of this order of magnitude, varying according to treatment from ·0001 to ·006 per cent. Complication arises from the fact that the plant takes up the greater part of its nutrients from the soil during its early days, so that a concentration which is appropriate and necessary at one period of its life is not suitable at another. This branch of the subject has been much investigated in the United States, and we are fortunate in having a paper by Dr. Hoagland, one of the foremost investigators. The physico-chemical problems associated with this solution arise out of its relationships to the soil particles on the one hand and absorbent root hairs on the other: they deal with the forces with which the solution is held to the soil or the root, and the effect of the soil and the plant on its composition. The magnitude of the forces has been measured by Dr. Shull, who gives his own account in the paper he has been good enough to send. It is now recognised that at least three kinds of forces are acting: intimate molecular forces of a magnitude of 1000 atmospheres or more, capillary forces, and gravity. The pull of the plant is considerable, coming in magnitude between the capillary forces and the molecular forces. Formerly it was supposed, and evidence was not lacking, that definite transition points existed between which the soil water could be described as being in a certain definite state—the hygroscopic state, capillary state, and gravitational water. Keen has shown, however, that the evidence is faulty, and that there are no transition points and no breaks, but that the state of the water is represented by a continuous curve from saturation down to dryness: all the forces are acting all the time, though it is still true that over certain parts of the water curve one force may be more in evidence than others, thus impressing its general characteristics on the curve.

The work of Keen and of Shull affords evidence of the existence of colloids in the soil, although it does not enable us to say precisely in what form they exist. But it is clearly shown that soil differs fundamentally from a collection of sand grains, and that the existence of colloids must therefore be assumed.

The qualitative relationships are more complex. Soil particles possess the power of absorbing many soluble substances from their solutions. The simplest case is afforded by organic compounds of high molecular weight, such as dye-stuffs, etc., the absorption was at first supposed to proceed in substantially the same manner as is shown by colloidal substances: it was therefore regarded as an adsorption and used as a measure of colloidal material in the soil. Later work has shown that the phenomena are more complex.

Inorganic salts present greater difficulties because of the possibility of chemical reaction between some of the ions. The experimental facts are that PO_4, Ca, K ions are absorbed, but NO_3, SO_4, Cl are not. Further, the absorption of inorganic ions by the soil is much affected by the composition of the soil, and is quite different according as reactive calcium compounds are present or not. A distinction is made by German writers between "absorptively saturated" soils, which contain much calcium, and "absorptively unsaturated" soils, which do not: in practice the soils are distinguished by the fact that the "unsaturated" soils readily absorb the basic radicles from salts leaving the acid radicle or forming an aluminium salt, and therefore causing the solution to become acid. This is one factor in determining the "acidity" of soil with which Professor Sven Odén, Dr. Salisbury and Mr. Crowther will deal. Such soils exert a strong pull on the nutrients supplied to the plant and hence there arise manurial peculiarities which are at first sight puzzling, such as the remarkable effectiveness of calcium salts, etc. In certain special conditions the absorption or precipitation of substances from the soil solution is not general over the whole soil, but is localised, occurring at one level only. This produces a dense precipitate through which water does not readily find its way: it is known as a "pan" and it has to be broken up by cultivation before satisfactory growth can take place. Mr. Morison has studied this special case in detail.

With a little ingenuity it seems possible to explain on purely chemical grounds the difference between absorptively saturated and unsaturated soils, but the general properties of absorption show so many similarities to absorption by colloids that the action can be and has been attributed to soil colloids. Again, however, it is possible for an ingenious chemist to show (as E. A. Fisher has done) that the phenomena of absorption are explicable on purely chemical grounds. A chemist can allow himself considerable latitude, as remarkable chemical changes do go on in the soil, such for instance as the decomposition of phenol, of potassium sulphocyanide, the conversion of calcium cyanamide into urea. Undoubtedly some soil constituents are very reactive. It is undeniable that chemical changes could, and probably do, take place, but these would be quite consistent with a preliminary physical absorption. Van Bemellen's arguments seem very cogent. And if on other grounds it is necessary to assume the presence of colloids we cannot ignore them or deem them non-existent for purposes of absorption: we must take them into account.

THE PHYSICAL PROPERTIES OF THE SOIL IN RELATION TO SURVEY WORK.

BY G. W. ROBINSON, M.A., ADVISER IN AGRICULTURAL CHEMISTRY,
UNIVERSITY COLLEGE OF N. WALES, BANGOR.

Considerable difficulty has been experienced in the correlation of plant and soil surveys. This may be attributed to a large extent to the defects of existing methods of soil classification. In the classification of any material, whether soils, plants or animals, the method to be adopted is to a large extent arbitrary. For example, soils may be classified on a purely genetic basis and, from the geological point of view, this classification is the one naturally to be adopted. From the point of view of plant physiology, however, a genetic classification may be of little use.

In many regions the genetic classification proves quite satisfactory even from the point of view of plant physiology, and the properties of a soil may be closely correlated with the conditions of its origin. Geology and climate are the principal factors in soil formation. Under conditions such as obtain over most of England and Western Europe generally, the influence of geology on soil is well exemplified. Hall and Russell in their survey of the soils of Kent, Surrey and Sussex, were able to classify soils satisfactorily on a geological basis. Under more extreme conditions of climate as exemplified by the semi-arid regions of South-Eastern Europe and the extreme humid regions of our own islands the influence of geology on soil is much less marked. Accordingly, we find the Russian school of soil workers classifying soils largely on a climatic basis.

Working in North Wales, the writer has found the correspondence between geology and soil much less marked than in England. The rather extreme humid conditions may account for this to a large extent. Other observers have noted that under extreme conditions of climate, whether of temperature or rainfall, the influence of the parent rock is reduced to a minimum. The lack of correlation between geology and soil need not, however, prevent the investigator from establishing soil types. The question of course arises whether soil types always exist, or whether in some cases soils are unclassifiable. In some districts, the isolation of soil types is an impossible task. Among the glacial soils of certain districts of North Wales, it is possible to find a continuous gradation from sands to clays without any definite grouping. In other areas soil types do undoubtedly exist, and a large number have already been described.

This leads to the question of the criteria used in soil classification and the isolation of soil types. At present, mechanical analysis is the general criterion used for the characterisation of soils. In this country the soil is separated into six grades of particles, varying from fine gravel to clay. There are, however, throughout the world, a large number of different conventions as to the limits of the size of the different fractions. Uniformity is impossible as each country has accumulated too many data to effect a change. It is thus impossible to compare an English soil with, say, a Hungarian or a Swedish soil. Even in the case of the clay fraction where the upper diameter limit is taken as ·002 mm., any comparison is vitiated by the different methods of separation in use. Another drawback to mechanical analysis, namely, the discontinuity of grouping, has been overcome by the elegant apparatus devised by Sven Odèn, whereby the mechanical analysis of a soil can be expressed as a continuous curve.

The main defect of mechanical analysis, however, as a basis for soil classification is that it only gives information as to the properties of the soil by inference. The mechanical analysis will tell us little about the properties of the soil beyond what is contained in the practical man's classification into sands, loams and clays. Indeed, within certain limits, the same information might be gleaned by the ordinary methods of silicate analysis. In other words the information given by mechanical analysis only differs in degree from that given by chemical analysis. The formula of an organic compound describes its constitution, but its properties are given by such constants as melting-point, boiling-point and refractive index. The mechanical analysis of a soil is analogous to the constitutional formula of an organic compound.

Mechanical analysis is of undoubted value from the point of view of the genetic classification of soils. It enables the investigator to group together soils of similar origin. Apart from its diagnostic value, it gives certain indications as to the actual properties of the soil, but these are only imperfect and indirect. Attempts have been made to correlate cropping with mechanical analyses. The correlation is, of course, complicated by climatic and economic factors, but even allowing for these, the correlation obtained is imperfect, and it may be doubted whether the mechanical analysis of soil can do more than standardise the practical man's classification of soils into heavy, medium and light.

It is probably this defect in mechanical analysis which is responsible for the disappointing results obtained from soil surveys. Soil survey work has been in progress in this country for fifteen years or more, while ecological studies have been carried on for an even longer period. Yet the actual progress in the correlation of plant and soil surveys is almost negligible.

In North Wales one frequently finds tracts where the edaphic conditions as indicated by the natural vegetation vary sharply from point to point without any apparent change of soil type. Differences in the air and water conditions of the soil are probably the main factors causing these variations, but there is no reliable quantitative method of expressing them. The mechanical analysis is almost useless, and can only occasionally be correlated with the natural vegetation. I am speaking, of course, of a province where the climatic conditions are somewhat extreme, but the same difficulty must frequently arise in districts of more moderate rainfall.

In the opinion of the writer, the only remedy for this and the only way to get a fresh impetus for the field study of soils is to examine the soil from the point of view of its actual properties. To say that a soil contains 20 per cent. of clay does not give a picture of the actual properties of the soil except by inference. In fact, certain materials, such as kaolin and finely ground slate, give as much clay by mechanical analysis as fairly heavy soils, although they lack the characteristic property of clays, namely, plasticity. Further, among the plastic clays the amount of clay by mechanical analysis cannot be correlated completely with the texture.

Although the original data of mechanical analysis are quantitative, the deductions from them are certainly not quantitative. The most valuable data about the soil are those which give direct information as to the properties of the soil as they affect plant life. In the opinion of the writer, the data in question would be given by a series of physical constants comparable to those which are indispensable to the description of a newly discovered element or compound.

An example of this method of investigation is furnished by Atterberg's work on the plasticity of soils. From the agricultural point of view, information as to the working properties of a soil is highly desirable and the figures given by Atterberg's methods are of direct importance. His "Plasticity Number" gives the range of water content over which a soil is plastic, while the figures obtained by him for the cohesiveness of soils (festigkeit) give direct information as to the resistance of the soil to comminution by the ordinary operations of tillage.

Pore space as a physical constant for the soil would be of considerable use. Owing to the difficulties of obtaining a sample of the soil without disturbing its field structure, a satisfactory routine method for determining this value has not been devised. The methods of Kopecky and Trnka are instances of attempts to solve the problem. Could a satisfactory method be devised, it would be easy to determine to what extent it is specific for a given soil and to follow the variations due to season and soil treatment.

Closely connected with pore space is the determination of water-holding capacity. Here again some confusion reigns, partly due to the same difficulty of obtaining a sample with unaltered field structure. A constant to represent the permeability of soil for water and air would be of considerable value. Green and Ampt's methods, if they could be applied to investigation of natural soils, would be very suitable. The specific surface of soils has undoubtedly a physiological significance as a measure of the degree of dispersion. The methods of Mitscherlich, Hilgard, and others for the measurement of hygroscopicity are worthy of attention, and it ought to be possible to devise some rapid routine method applicable to the study of soils on an extended scale. The problem has also been attacked by measuring dye absorption. In the opinion of the writer this method is not to be recommended as it is liable to be complicated by chemical reactions between the dye used and soil constituents.

There are, of course, other physical properties of the soil on which quantitative ideas are needed, and it is to be hoped that the recognition of soil physics as a branch of investigation at Rothamsted will lead to a useful development of the work begun in this country by Warington.

Whatever physical measurements may be devised for the investigation of soils, there are certain desiderata if they are to be of use in field study. Firstly they must deal with the soil in its natural structure. The soil of the laboratory is an artificial product. Results obtained on it are apt to be misleading on the chemical side and even more so on the physical side. The methods devised should also be capable of being repeated in large numbers. The soil is such a complicated object of study that statistical methods must to a large extent remedy the unreliability of single observations. Methods to be devised for the physical investigation of the soil may have to sacrifice a little accuracy in order to make it possible to multiply observations in large numbers for the purposes of statistical treatment.

If reliable methods could be devised for characterising the physical properties of soils by a series of physical constants, the edaphic classification of soils might be placed on a much surer basis than at present and correlation with vegetation and agricultural conditions might be expected. The physical properties of a soil as expressed by such a series of constants would be of importance from the point of view both of plant physiology and of practical agriculture, since they would give quantitative expressions for factors which directly affect edaphic and cultural conditions. Supplemented by a few chemical and economic data, the agricultural properties of a soil could be completely characterised.

The investigation of the physical properties of the soil must in future be one of the most promising lines of inquiry. The soils of our country do not as a rule show any striking deficiencies in plant food capital and such deficiencies as do occur are easily made good. The ultimate productiveness of our soils is largely a matter of physical properties. With the new impetus given to the physico-chemical study of soils of which this discussion is an evidence, it may be expected that the routine methods in use by field investigators will be more in the nature of physical determinations than of chemical analyses.

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April 27th, 1921.

Summary.

The classification of soils with the aid of mechanical analysis is of use mainly from the genetic standpoint. Apart from the defects of this method of examination and the lack of uniformity of procedure in different countries, the information given by such analyses is of comparatively little value in characterising the actual properties of the soil other than by standardising the ordinary practical classification into sands, loams and clays. Correlation with edaphic and cultural conditions is consequently imperfect. An edaphic classification should be based on actual soil properties, and for this purpose the soil might be better characterised by a series of physical constants comparable to those used in the description of a newly discovered element or compound. These constants might be supplemented by chemical data, but as it is easier to increase the amount of plant food in the soil than to change its intrinsic physical properties, physical constants would give a better definition of the inherent capabilities of a soil.

The soil is an exceedingly complicated material, and the lack of reliability of studies on individual soils necessitates the use of statistical methods. Determinations of physical properties must therefore be of such a character that they can be rapidly carried out on large numbers of soils. For many of these determinations, the soil must be examined without disturbing its original field structure.

Among the principal physical properties of the soil which affect edaphic and cultural conditions are pore space, water-holding capacity, permeability to water and air, plasticity and cohesion. Mechanical analysis must still be used as an aid to the genetic classification of soils.

SECTION II.—PAPERS AND DISCUSSION ON "SOIL MOISTURE".

THE SYSTEM SOIL-SOIL MOISTURE.

By Bernard A. Keen, B.Sc., F.Inst.P. Goldsmiths' Company's Soil Physicist, Rothamsted Experimental Station.

The system soil-soil moisture is exceedingly complex. On the one hand there is the soil—a mass of particles of all shapes and sizes, of varying chemical composition, and intimately associated with both organic and inorganic colloidal materials; on the other hand there is the soil moisture, holding in solution certain substances, some of which are essential, others detrimental, to plants and organisms. The system as a whole is subject to ever-changing meteorological conditions, as well as the effects of growing vegetation and organisms, and, at frequent intervals, abrupt changes in many factors occur owing to manurial and cultivation operations. Practically all of the factors are interdependent—if one of them changes, the remainder will also change in the necessary amount to suit the new conditions.

Another way of stating this is that soil phenomena are dynamic in character, not static.

When the relations between the soil and its moisture content were first examined the obvious hypothesis to take as a starting point was that the moisture was distributed in a thin continuous film over and around the soil particles. This view was eventually set out by Briggs (1) over twenty years ago, who treated the water films from the standpoint of the surface tension over their curved surfaces. This treatment is closely modelled on the well-known experiments of Reinold and Rücker (2) on soap bubbles which hardly need further mention here. It is instructive, however, to consider one case. Imagine a long row of wet spheres each of the same radius and touching one another, and let the row be raised from a horizontal to a vertical position. The liquid will drain downwards and drip from the bottom sphere. When equilibrium is established, the curvature of the annular ring of water between adjacent spheres will diminish, and the actual volume of this ring will increase from top to bottom of the row, the difference of pressure between adjacent rings being that necessary to support the weight of the film connecting them. Hence in a cylinder of moist soil, made up of coarse particles, there is a progressive increase in moisture content from top to bottom; in a finer soil this gravitational effect is much less marked owing to the smaller interstices between the grains. For each case, however, and for a given depth of soil, a distinction can be drawn between gravitational water, which drains away under the action of gravity, and capillary water, which is capable of movement over the soil particles under the forces of surface tension, whenever the equilibrium is disturbed. Briggs further distinguishes hygroscopic water, which, as the name implies, is the thin film of condensed vapour deposited on soils when in the presence of water vapour. This hygroscopic moisture is held with considerable force, and is presumed to be incapable of movement under capillary and gravitational forces.

The classification of soil moisture into hygroscopic, capillary and gravitational water is too broad to afford a clear picture of the moisture relationships in most soils, and it suffers from the defect that a soil is regarded essentially as a mass of sand grains which functions mainly as an inert framework over which the moisture film is distributed. A perusal in chronological order of the literature on soil moisture clearly shows—although explicit reasons were seldom given—that investigators considered the classification incomplete, and attempts were made to remedy this. Two courses were possible: to examine the above three divisions of soil water in greater detail, or to introduce a number of "equilibrium points" which would give a certain precision to the relations between the soil and its moisture content, when the latter varied over a wide range.

Taking the "equilibrium points" first, we may mention the "moisture equivalent" introduced by Briggs and McLane (3), and the "wilting coefficient" due to Briggs and Shantz (4). The former is defined as the amount of water retained in soil previously saturated, when subjected to a centrifugal force 3000 times the gravitational force.[1] This force is supposed to remove the water held in the larger capillary spaces of the soil; the amount of water remaining—the moisture equivalent—gives a single figure which expresses the power of a given soil to retain water under these conditions. Comparison of different soils on this basis is relatively simple. The moisture equivalent shows up the effect of both organic material and the clay fraction in increasing the water-holding power of the soil, and therefore gives more precision to the relations between soil and water:—

Moisture Equivalents of Six Soils (Briggs and McLane).

Vernon sand	3·6
Vernon fine sand	4·3
Vernon sandy loam	10·3
Vernon fine sandy loam	12·3
Vernon silt loam	19·8
Vernon clay (loam)	23·1

The method apparently does not suffer to any appreciable extent from the defect of many methods of soil examination—the disturbance of the packing of the soil grains as it exists in the field. This disturbance mainly affects the larger pore spaces, but not necessarily the smaller ones associated with the soil aggregates or compound particles, and as we have seen it is these latter which are of importance in the determination of the moisture equivalent.

The "wilting coefficient" is an attempt to correlate the requirement of the plant for water and the power of the system soil plus water to supply it. The assumption is that the roots of any given variety of plant can exert a definite maximum pull on the soil moisture, which will be given up by the soil to the roots less and less readily as the moisture content of the soil decreases. Eventually a point will be reached at which the soil will not part with further water and the plant wilts. The percentage of water in the soil when permanent wilting of the plant occurs, is defined as the "wilting coefficient". Like the moisture equivalent the wilting coefficient increases with increasing fineness of the soil particles, and under the experimental conditions which Briggs used, it is largely independent of the kind of plant used, and has a value a little over half the figure for the moisture equivalent:—

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[1] This value was chosen as the most convenient after a series of experiments with different speeds of centrifuging. Over a fairly wide range a linear relation existed between the moisture equivalent and the reciprocal of the centrifugal force.

Wilting Coefficient for Kubanka Wheat (Briggs and Shantz) *in*

Fine sand	Fine sandy loam	Clay loam
2·59	9·66	16·3

It will readily be seen that if these two "equilibrium coefficients" be true ones, they will help considerably in forming a mental picture of the relations between the soil and its moisture content. The wilting coefficient has been investigated both by Alway (5) and Shull (6) among others, who give reasons to doubt the validity of its conception—at least in its original form. Alway showed that plants could live in soil containing less water than the wilting coefficient if the atmospheric conditions were modified; they could in fact utilise the water down to the hygroscopic coefficient, which as we shall see later is, according to Briggs, only ·7 times the wilting coefficient.

Shull's work was undertaken to find some means of measuring the force with which particles of soil of varying fineness retain moisture at different degrees of dryness, and to obtain information on what may be called the "back-pull" of soil when its moisture content is so low as to be unavailable to growing plants. Especial interest, therefore, centres in the conditions occurring in the region around the wilting coefficient. Advantage was taken of the discovery of Brown (7) and others, that certain seeds have semi-permeable coats, and *Xanthium* seeds were taken because of their rapid establishment of moisture equilibrium after a disturbance. The experiments fell into two sections. First of all, the amount of water taken up by air-dry seeds under various osmotic pressures was determined. This was done either by immersing the seeds in salt solutions of known osmotic pressure, or by suspending the seeds over the vapour of sulphuric acid of known strengths and then calculating the corresponding osmotic pressure of the acid by means of Walkers' equation connecting osmotic and vapour pressures. These experiments gave values for the osmotic pressure at different moisture contents of the seeds.

The second group of experiments consisted in allowing the dry seeds to come to moisture equilibrium with soil, moistened to different degrees. Having determined the percentage of moisture in the seeds and soil when equilibrium was attained, the corresponding osmotic pressure of varying percentages of soil moisture is obtained at once from the first set of data. Comparison of the results in the region of the wilting coefficient leads to some interesting conclusions: firstly, seeds take up nearly as much water from soil whose moisture content is equal to the wilting coefficient as they do when placed direct into water, and, secondly, in soil at this moisture content, the osmotic pressure is not more than 3-4 atmospheres. Now the average root-cell sap pressure is 7-8 atmospheres. The plant wilts, therefore, although both the amount of soil moisture and pressure gradient are in its favour. The explanation of this apparent anomaly is that evaporation continues from the leaves of a plant somewhat regardless of the conditions below the soil surface. At the wilting coefficient the rate of movement of soil water falls below that needed to maintain the turgidity of the aerial parts of the plant, which consequently wilts.

The conclusion to be drawn from the work of Alway and Shull discussed above is that the wilting coefficient is not a definite constant for a given soil but is made up of complex factors in which the soil, the plant, and the atmospheric conditions all enter.

Leaving for the moment questions dealing with the wilting point and moisture equivalent, we will briefly consider the other direction in which attempts were made to remedy the incomplete nature of the classification of soil moisture into hygroscopic, capillary, and gravitational divisions. This was an examination of the divisions in greater detail. The hygroscopic water has been studied by many workers (8) most of whom have considered the soil as a whole, and taken the value of the hygroscopic coefficient as a measure of the power of that soil to absorb water vapour. Little work has been done on the relative absorbing powers of different portions of the soil complex. Yet it is obvious that different portions may take up water in very different ways. There may be surface condensation on the non-colloidal portion, adsorption and imbibition by the colloids, and chemical effects, such as hydrolysis, especially with the organic matter. Hygroscopicity is therefore a complex phenomenon, but, in view of the importance now attached to the colloidal properties of soil, the subject could profitably be re-opened. There is ample scope for work in at least two directions: firstly the development of similar statistical studies to those of Luxmoore (9) on Dorset Soils, in which the hygroscopicity of a large number of soils is correlated with other physical properties; and secondly, an extension of Mitscherlich's (10) investigations on the amount of vapour absorbed by soil placed over a number of different liquids. Mitscherlich uses 10 per cent. sulphuric acid, and one of various organic liquids of high molecular weight. The vapour of the latter is supposed to condense only on the outer surface of the compound particles, or soil crumbs, whereas the water vapour from the sulphuric acid condenses both on the outer and internal surfaces of the crumbs. Comparison of the two values for different soils enables an estimate to be made of the extent to which the soil is aggregated into compound particles, and the method, therefore, is likely to be of use in extending our present scanty knowledge of the relation between good tilth and the formation of compound particles. At the same time a parallel series of experiments could be done on the "heat of wetting," following the work of Müntz and Gaudechon (11). These workers found that the greater part of the heat evolution when water was added to dry soil was due to the colloidal portion of the clay.

Heat Evolved on Wetting a Soil and its Component Fractions.

(Müntz and Gaudechon.)

Soil Fractions (after Kopecky).	Percentage of Fractions Present in Soil.	Heat Evolved by 1 Kilo. of each Fraction.	Calculated Heat Evolution for Percentage of Fraction Present.
Coarse sand > ·1 mm.	11·30	0·0 kilo-calories	0·0 kilo-calories
Fine sand ·1-·05 ins.	16·52	0·26 "	0·04 "
Sandy silt ·05-·01 mm	44·89	0·64 "	0·28 "
Clay silt < ·01 mm.	27·29	3·1 "	0·84 "
Total . .	100		1·16

Experimental value for the soil 1·14.

The organic matter, weight for weight, was even more effective, but the major portion of the heat evolution is due to the clay, owing to the small amount of organic material present in most soils. Mitscherlich (12) did some work on the relation between heat of wetting and the hygroscopic coefficient of soils, but could find no apparent connection. The whole subject could profitably be reopened in the light of present knowledge.

The hygroscopic water, although of great importance in physical studies of soil, is not directly of use to growing plants, and probably for this reason the next division of soil water—the capillary film—has received more attention. Both the wilting coefficient and the moisture equivalent already mentioned lie in this region. Especial interest attaches to the lower, and to a lesser degree the upper limits of capillary water. The former limit has been examined by Widtsoe and McLaughlin (13) in connection with irrigation studies in Utah. As already mentioned, a soil containing water only slightly in excess of the hygroscopic coefficient supports plant life with difficulty, and, on the water film hypothesis of soil moisture, this is because the movement of water in the soil is very slow at this moisture content. Widtsoe and McLaughlin consider that the point at which moisture movements become very sluggish can be ascertained from determinations of moisture content after irrigation. They call this point the "lento-capillary point" and define it as "the point at which capillary movements largely cease, and at which plant roots must secure water through greater effort, by actual contact with the water holding particle, or possibly by thermal transference of water".

In addition to the hygroscopic coefficient and the lento-capillary point, Widtsoe and McLaughlin also define the "maximum capillary water capacity" and the "optimum capillary water capacity" or field water capacity. Water present in excess of the former—which has a value of 24 per cent. for the soil used—is assumed to be free water, while the latter represents the amount of water found in the irrigated soil when full distribution has occurred. Its value is about 18 per cent. for the soil used, and it indicates the most favourable percentage of moisture for plant growth. Practical men recognise a comparatively narrow range of moisture content for any given soil, within which plants attain their maximum development; below this range there is insufficient water, and above it the additional water necessarily restricts the air supply.[1] The optimum capillary water capacity is an attempt to give a physical significance to this value. Numerous studies have been made on it, among which the work of Cameron and Gallagher (14) may be mentioned. They had the help of several experienced greenhouse men, to decide by inspection when each soil was at its "optimum moisture content" for plant growth. Various physical properties, such as apparent specific gravity, cohesion, penetrability, rate of evaporation of water, and so on, were measured for each soil at different moisture contents, and the results indicated that these properties passed through either a maximum or a minimum at the optimum moisture content.

In addition to the various constants already mentioned, there is a further one, known as the "maximum water capacity". This is simply a measure of the pore space in the soil, under the experimental conditions. The best known method is that devised by Hilgard (8) which consists essentially of saturating a thin layer of soil, from below, to expel as much air as possible, and measuring the increased weight due to the water. The value is always in excess of the maximum found in the soil under field conditions, for obvious reasons.

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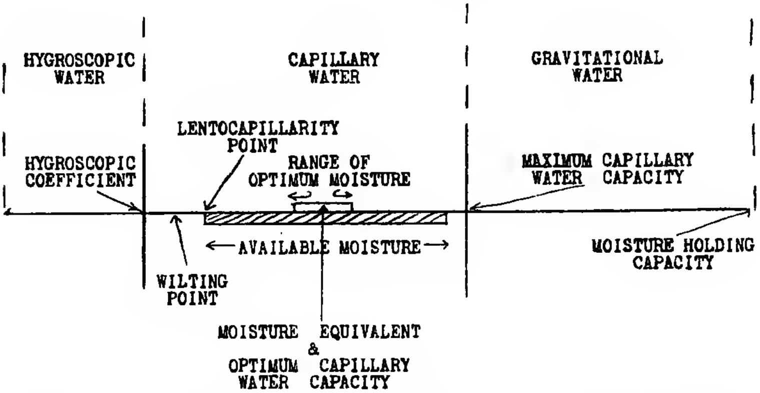
[1] The influence of soil aeration on plant growth has been studied by A. Howard and G. L. C. Howard. See Bulls. 52 (1915); 61 (1916), Agric. Res. Inst., Pusa.

The original divisions of soil moisture and the further sub-divisions and equilibrium points may be diagramatically represented as follows:—


HYGROSCOPIC WATER
CAPILLARY WATER
GRAVITATIONAL WATER
LENTOCAPILLARITY POINT
HYGROSCOPIC COEFFICIENT
RANGE OF OPTIMUM MOISTURE
MAXIMUM CAPILLARY WATER CAPACITY
←AVAILABLE MOISTURE→
MOISTURE HOLDING CAPACITY
WILTING POINT
MOISTURE EQUIVALENT & OPTIMUM CAPILLARY WATER CAPACITY

Obviously, there has been considerable elaboration of the original divisions, but a general criticism of the scheme can yet be made: the additional divisions and equilibrium points have no very obvious relations with each other—they resemble a series of water-tight compartments—nor is there any clear indication of the relations between the soil and the moisture content. Attempts were made to remedy this. The work of Cameron and Gallagher, already mentioned (14), brought out the interesting point that the moisture equivalent was very approximately equal to the optimum moisture content. Briggs and his collaborators (3; 4) introduced a series of cross relations between some of the equilibrium points, and studied the effect of the soil type upon them. They arrived at the series of relations shown:—

(Briggs and Shantz.)

(The second term in the brackets shows the probable error of the relationship.)

$$\text{Wilting coefficient} = \frac{\text{moisture equivalent}}{1{\cdot}84(1 \pm 0{\cdot}007)}.$$

$$\text{,, \quad ,,} = \frac{\text{hygroscopic coefficient}}{{\cdot}68(1 \pm 0{\cdot}018)}.$$

$$\text{,, \quad ,,} = \frac{\text{moisture holding capacity }(a) - 21}{2{\cdot}90(1 \pm 0{\cdot}021)}.$$

$$\text{,, \quad ,,} = \frac{0{\cdot}01 \text{ sand} + 0{\cdot}12 \text{ silt} + 0{\cdot}57 \text{ clay }(b)}{(1 \pm 0{\cdot}025)}.$$

(*a*) Hilgard's method. "Soils" (1906), p. 209. New York.
(*b*) Sand ·2 to ·05 mm. in diameter.
Silt ·05 to ·005 ,, ,,
Clay $<$ ·005 ,, ,,

The primary purpose of these ratios was to enable the wilting coefficient —a troublesome thing to determine experimentally—to be calculated from more easily obtained soil constants, the tacit assumption being made that a linear relationship exists between the variables. A similar assumption led to the following expression connecting the moisture equivalent with the type of the soil as defined by its mechanical analysis:—

$$0{\cdot}4\,C + 0{\cdot}59\,D + 0{\cdot}53\,E = M \pm 1{\cdot}1$$

where M = moisture equivalent
C = percentage of particles ·05-·005 mm. in diameter
D = ,, ,, ,, below ·005 ,, ,, ,,
E = ,, ,, ,, organic matter.

The soils to which this equation refers are a typical and well-defined series derived mainly from one geological source. For another series the coefficients, in general, have a fresh set of values, although these referring to the clay fraction D and the organic matter E do not differ greatly from one another. This indicates that clay and organic matter weight for weight have equal influence on the moisture equivalent. The influence of particles of larger size than group C is very small—a change of 50 per cent. in the amount of coarse sand resulting in a change of 1 per cent. in the moisture equivalent.

These attempts of Briggs to link into a coherent whole the various divisions and equilibrium points have been subjected to criticism. It could hardly be expected that a series of cross relationships based on the assumption of a linear relation between the variables would suffice to specify the complex system soil-soil moisture, but a certain degree of approximation might be expected in some cases. Alway and his collaborators (15) have already made a long series of valuable studies on the subject, and typical papers are given in the attached bibliography. It is impossible to give an adequate summary of them here; they are mainly concerned with the relations of the soil constants mentioned above, to the amounts of water found, and its rate of movement in the soil under certain conditions. Those who wish to pursue the matter further will find a discussion of Alway's results in a recent paper by the present writer (16). Generally speaking, the results show, as in the case of the wilting coefficient mentioned earlier, that the equilibrium points and sub-divisions need to be interpreted with caution, because they are not necessarily by themselves a reliable specification over the wide range of moisture content met with in soil.

However, if the constants are to have any significance at all, beyond a somewhat indirect and qualitative physiological one, some fundamental hypothesis must be found which shall account for them all and, at the same time, show their relationships to the behaviour of moisture under field conditions.

Taking a broad view of the problem it is suggestive to treat the movement of moisture in soil on analogous lines to the flow of heat and electricity. This implies the existence of a capillary transmission constant, or potential factor, which will enable us to calculate the flow of soil moisture between two places of different moisture content, in the same way that the thermal conductivity, and a knowledge of the temperature at two points in a solid, enable us to calculate the heat flow. A pioneering investigation along these lines was published by Buckingham (17) in 1907, and recently Gardner (18) has reopened the problem. The mathematical treatment is somewhat difficult, because in practice the capillary transmission "constant" is itself a variable function, but Gardner has been able to obtain encouraging agreement between theory and experiment in a number of cases. The underlying idea in the work, as expressed by Gardner, is that "a knowledge of the functional relation between the potential, the moisture content, and the effective radius of the soil particle, whether obtained empirically or by theoretical speculation, would not only be equivalent to a knowledge of the various moisture constants, but also relations that may exist between them, such as the Briggs system of equations," to which reference has already been made (3; 4).

These investigations of Gardner are still in their early stages. It is apparent that one of the greatest difficulties in the work will be the derivation of a proper function to represent the capillary potential in the differential equations for water movement. It is quite certain that the original hypothesis regarding the soil as a framework of inert sand grains will be insufficient for this purpose; the effects of the colloidal material in the soil must be included. The modern hypothesis—which seems to have been first put forward in definite form by J. Dumont (19) is that this colloidal complex, derived both from inorganic and organic material, may be regarded as a coating around the soil particles, especially those of smaller size. This coating can hardly have a definite outer surface. It may be considered as surrounding the soil particle in a series of shells of gradually increasing hydration as Hall (20) has suggested, so that there is a continuous transition from a solid nucleus to soil solution. With regard to the relation of the coating to the root hairs of plants, Comber[1] has put forward an interesting suggestion to explain the well-known difficulty of washing the roots entirely free from small soil particles. It is suggested that the root hair makes an indissoluble attachment with the colloidal coating of the particle, the outer wall of the cell being converted into a mucilaginous substance. The possibility therefore arises that the plant may be able to absorb directly colloidal substances from the soil.

The constitution of this soil colloidal complex is as yet largely unknown, and even the percentage of it present is uncertain. The classical experiments of Schloesing (21) and the recent repetition of the work by Ehrenberg and Given (22) gave figures of 1-2 per cent., while experiments of Tempany (23) based on the shrinkage of moist soils when dried, led to much higher values. In some soils nearly the whole of the clay fraction seemed to be in the colloidal condition. In the majority of soils there is reason to believe that the colloidal constituents derived by weathering and other agencies from the soil particles—the inorganic colloids—are mainly responsible for the effects observed. Possibly the organic matter, weight for weight, produces effects of the same order as the clay, but the latter is usually present in excess, and in any case the inorganic and organic colloids are so intimately mingled in the soil, that it is very difficult to ascribe separate functions to them. Information can be obtained, however, by using an extreme type of soil. This has been done by Crump (24) who worked with moorland and peat soils, and examined the ratio $\frac{\text{water content}}{\text{humus content}}$ which he calls the "coefficient of humidity".

The values for this ratio were obtained as follows:—

Water content = weight when sampled—weight at 15° C.
Humus content = weight at 100° C.—weight after ignition.

Naturally, the variation in total moisture content due to meteorological conditions, will affect the value for the ratio, but a sufficient number of experiments will give a frequency curve from which the modal value may be taken as typical for the soil in question. Crump found that if samples were taken during the growing period of plants and not immediately after heavy rain, that the values for the coefficient of humidity of a given soil did not vary appreciably, so that the labour of taking a large number of samples was not necessary. An important fact brought out by the work was that the value of the coefficient of humidity is sensibly constant for different layers of a soil whose constitution alters greatly with depth:—

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[1] Private communication.

Values of the coefficient of humidity (Crump):—

Material.	Water at 15° C.	Humus.	$\frac{\text{Water}}{\text{Humus}}$.
(i) Humus at 1-2½ ins.	170·0 per cent.	55·5 per cent.	3·06
(ii) Sandy soil below (1)	30·4 „ „	10·4 „ „	2·92
(i) Black soil at ½-1½ ins.	67·4 „ „	33·4 „ „	2·01
(ii) Same at 1½-2½ ins.	40·3 „ „	18·6 „ „	2·16

The table shows that in spite of the wide difference in water content of two such layers, the coefficient of humidity is not sensibly different; from the point of view of the plant roots, both layers are equally moist. When the work was extended to a number of peat soils having the same habitat it was found that the values of the coefficient of humidity for these peats, although the samples were taken at widely different times, did not differ greatly from the mean value, and further, in the case of the sub-peats from the same localities a different, but still approximately constant value of the coefficient was obtained. It is apparent that Crump's work opens up a very promising field of research in ecological studies. It is important that similar investigations should be made on arable soils and permanent pastures, where the clay fraction has to be considered as well as the organic matter, in the valuation of the coefficient of humidity.

For our present purpose the main interest in the work is the demonstration of close relations between the moisture content and certain soil constituents possessing colloidal properties.

These relations have been demonstrated in another way by the present writer (25). A study was made of the evaporation of water from moist soil over sulphuric acid, using an apparatus devised to overcome experimental errors as far as possible. The results showed, in contradiction to some earlier work of Patten and Gallagher (26), that the evaporation curves for thin layers of moist sand and soil were different, and that, further, this difference was largely due to the colloidal property of the clay fraction. The evidence for this last statement was obtained from the evaporation curves (Fig. 1) given by a rich garden soil, which was divided into three portions, and treated as follows:—

Portion C: untreated, for control.

Portion B: soluble humus removed by extraction with 2 per cent. NaOH in the usual way.

Portion A: ignited to remove all organic matter and to destroy the colloidal properties of the clay.

The evaporation curve for portion B shows a slightly increased rate of evaporation, but the curve is not much different from that for portion C, whereas the curve for portion A is identical with that given by moist sand. Recently further experimental evidence has been obtained on the relative effects of organic matter and clay on evaporation by using soils which differ only in their manurial treatment. The results will shortly be published in full elsewhere, but it may be stated here that the differences due to manurial treatment are not so important as those due to the amount of clay in the soil.

The general conclusion is that the evaporation from soil under the experimental conditions is mainly controlled by the colloidal portion of the clay fraction; further, the evaporation curve is continuous, and shows no breaks or abrupt changes of direction. There is, for instance, nothing to indicate a rapid diminution of vapour pressure immediately below the optimum moisture content as deduced by Cameron and Gallagher (14). In fact, the rate curves for a soil containing about 20 per cent. of clay can be fitted over practically their whole range by an equation of the form :—

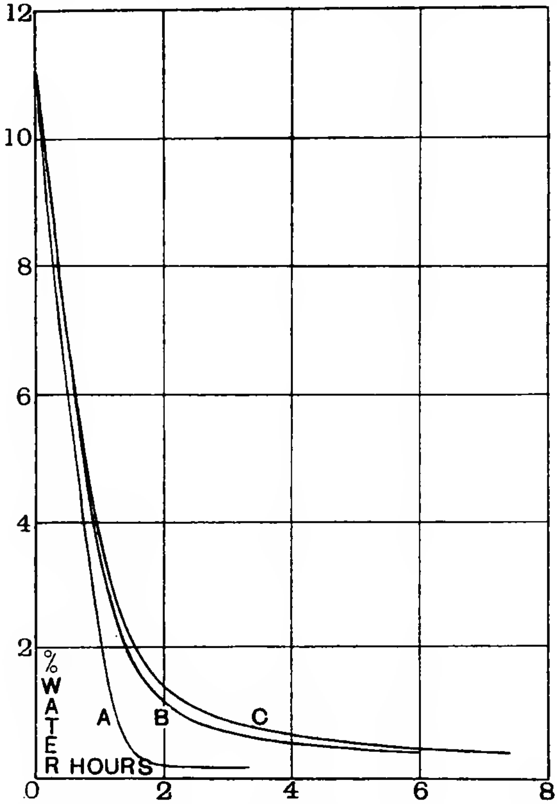


FIG. 1.

$$B\frac{dw}{dt} = \sqrt[3]{\left(\frac{ws}{100} + 1\right)}[2\cdot 303 \log (w + k) - \log_e k]$$

where $\frac{dw}{dt}$ = time rate of evaporation

w = moisture content (percentage on dry weight of soil)

s = true specific gravity of the soil

B and k = constants for each type of soil used.

The right hand side of equation contains two factors: that in square brackets is empirical, and in all probability is connected with the vapour pressure at different moisture contents. By itself it does not completely fit the rate curves, but when the second factor $\sqrt[3]{\left(\frac{ws}{100}+1\right)}$ is introduced, the agreement is very good. This factor expresses the effect of diminishing surface from which evaporation can take place as the soil dries out; the thickness of the moist film diminishes and hence its surface area diminishes also.

From the foregoing discussion it will be seen that, as agricultural science has progressed, the complexity of the relations between the soil and its moisture content has become more and more evident, and at the same time it has been realised that there is a continuity in these relations over a wide range of moisture content. It is perhaps appropriate to emphasise at this point that the ultimate value of any relations shown to exist between the soil and its moisture content will largely depend on the help they give to another great branch of agricultural research—the relations between the plant and the nutrient soil solution. The soil moisture containing various substances in solution, and possibly also in colloidal suspension, occupies, as it were, the central position; on the one side there is the soil, and on the other the plants and organisms.

In the above discussion we have consistently used the terms moisture or water, in accordance with the usual convention. The term soil solution could with more correctness have been used, although it is by custom employed only when special attention is being directed to the substances, soluble and suspended, in the soil moisture.

It is obvious that if we could remove the soil solution from the soil, we should at once be able to test a large number of important points connected with its relations with both the soil and plants. It is quite easy to remove liquid from soil of course, but it is another matter to say whether the liquid so removed is a true sample of the soil solution as it exists *in situ*. A large number of different methods have been described and their relative values discussed, and it is not proposed to consider them here. The reader is referred for this information to papers by Stiles and Jϕrgensen (27), Bouyoucos (28), Morgan (29), and C. B. Lipman (30). Neither is it proposed to consider the controversy on the composition of the soil solution, which centred around the deductions of Whitney and Cameron (31) that the soil solution is saturated with compounds of phosphoric acid and potash to the same low degree of concentration in all soils, and the well-known refutation of this idea set out by Hall, Brenchley and Underwood (32). It is sufficient to remark that the former hypothesis has been shown untenable in its original form, and that the composition of the soil solution does vary significantly from soil to soil, in general accordance with the soil type and its manurial treatment.

Investigations on the soil solution have recently been stimulated by the employment of two methods that enable the soil solution to be studied *in situ*.

These are the dilatometer and freezing point methods, and their adaptation to soils is due to Bouyoucos, who has developed them in a number of interesting papers (33).

The dilatometer experiments show that a certain proportion of the water in soil fails to freeze at a temperature of − 1·5° C. A certain amount of this "unfree" water can be frozen if the temperature is reduced to − 4·0° C., while some will not freeze at − 78·0° C. On the basis of these results Bouyoucos arrives at a new division of soil water, indicated in the scheme below. The relative proportions of the different groups vary from soil to soil. The physiological significance which Bouyoucos attaches to the different groups is also shown :—

Gravitational			"superavailable".
Free			very available.
Unfree	capillary-adsorbed . .		slightly available.
	combined	water of solid solution water of hydration	unavailable.

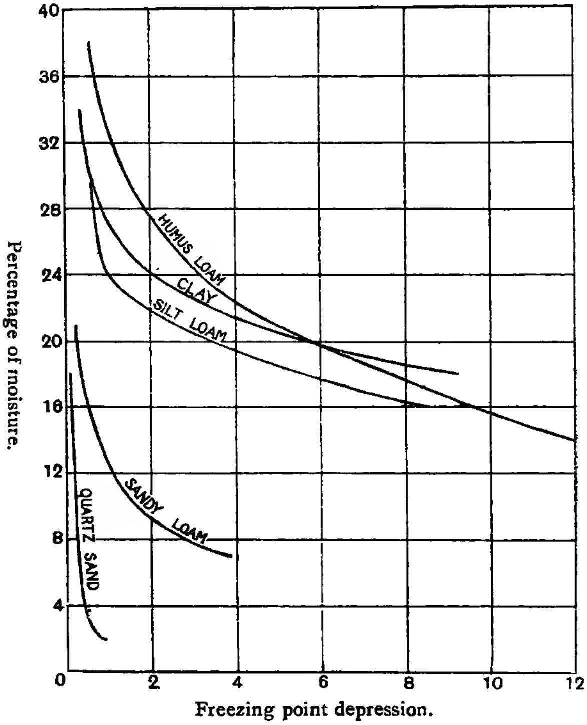
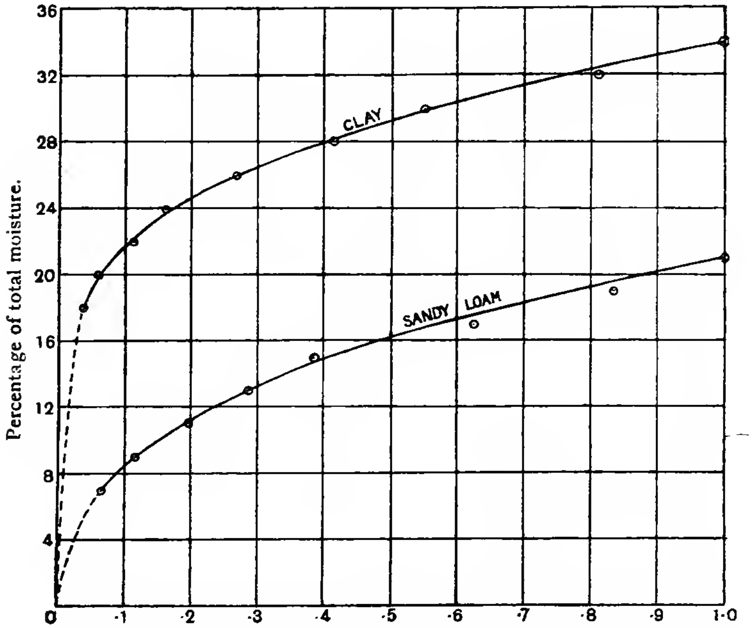


Fig. 2.—Increase in freezing point depression, with decrease in moisture content (Bouyoucos).

The freezing point experiments are done direct on the moist soils in the usual Beckmann apparatus, and the depression of the freezing point is measured for different moisture contents. In moist quartz sand, and some extreme types of sandy soil, where the soil solution would be very dilute, the depression of the freezing point was found to be inversely proportional to the water content. This points to the moisture in the sand obeying the same law as dilute solutions—the freezing point depression varying approximately as the concentration. With the majority of ordinary soils, this relation did not hold. It was found that the freezing point depression rapidly increased as the moisture content decreased (Fig. 2). Bouyoucos interpreted this to mean that in soils a certain part of the moisture was rendered "unfree," in the sense that it did not take part in the freezing point depression.

Both the dilatometer and freezing point experiments, therefore, supported the idea of "unfree" water bound in some way to the soil. Since the freezing point determinations were done at a variety of moisture contents the experimental results offered material which seemed suitable for quantitative investigation. This was carried out by the present writer (34) and led to a series of interesting results. The fundamental assumption was that the freezing point depression at any moisture content was proportional to the effective concentration. This effective concentration was necessarily taken as inversely proportional to the free water present, *i.e.* inversely proportional to the total moisture content minus the "unfree water".



Free moisture, in fractions of Y_{21} for sandy loam, and Y_{34} for clay.
FIG. 3.—Relation between free water and total moisture, for clay and sandy loam soils.

With this assumption the experimental results lead to a relation between the "free" and total moisture, shown for two soils in the curves of Fig. 3. Both these curves are fitted by an equation of the type

$$Y_n = cM_n^x$$

where Y_n = free water at total moisture content of M_n
c, and x = constants for any one soil.

Knowing that $M_n = Y_n + Z_n$, where Z_n is the unfree moisture, we arrive at the following equation for the relations between free and unfree water :—

$$Z_n = \frac{1}{c^{\frac{1}{x}}} Y_n^{\frac{1}{x}} - Y_n.$$

However, this equation contains an unknown quantity in the constant c, and cannot be used directly. But we can obtain a series of values for Z_n from Fig. 3. At the highest moisture content ($M_n = 21$) for the sandy loam soil, the free water Y_n obviously lies between 0 and 21. Let it be given any arbitrary value, say 15, or 9; we then get a set of values for Y_n at various known total moisture contents and therefore obtain, by subtraction, the corresponding values for Z_n, the unfree water. Fig. 4 shows the relation between free and unfree water for various assumed values of Y_{21}. It is not easy to say which of the four curves is most likely to be nearest the truth. One would hardly imagine that the lower two curves would apply, as they indicate a maximum in the unfree water when the total water is about 12-15 per cent. It is difficult to conceive any physical reason why the unfree water should show such a maximum, although it is suggestive to associate this point with the optimum moisture content of Cameron and Gallagher (14), already mentioned. Probably the higher curves of Fig. 4 are nearer the truth. These curves, since they are also satisfied by the same general equation as the other two, have also a maximum, but it is comparatively flat, and eventually corresponds to a total moisture content of a higher amount than the soil could take up, and therefore is not compatible with actual conditions.

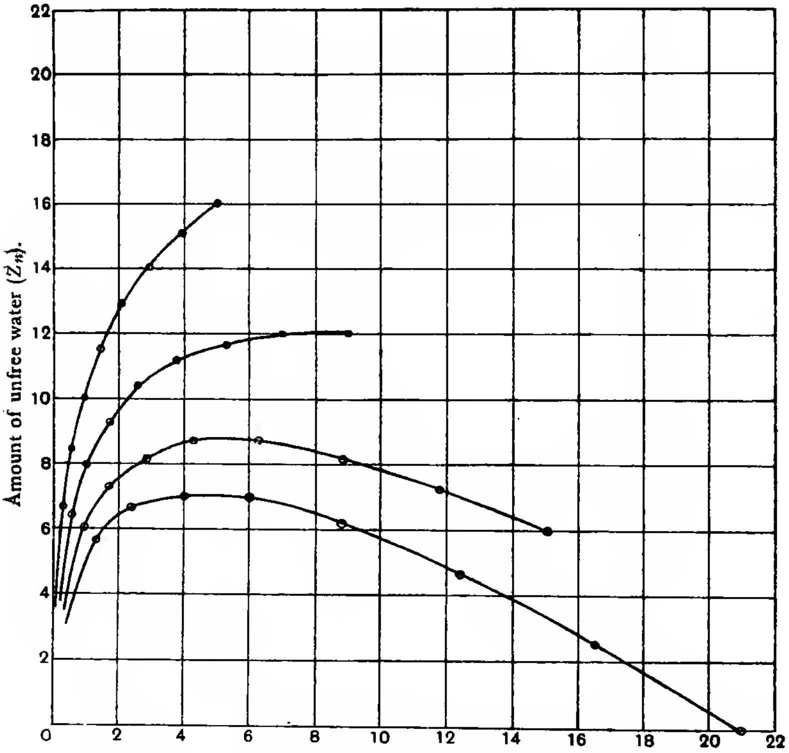


FIG. 4.—Relation between free and unfree water, for various values of Y_{21}.

It will be seen, however, that interesting and important relations hold between free, unfree, and total moisture content, if the assumptions underlying the application of the freezing point method to soil solution *in situ* are legitimate. Further, the results emphasise the continuous nature of the relations between soil and soil solution brought out in the writers' experiments on evaporation (25).

One very interesting point brought out by the curves is that the suggestion of Bouyoucos that the unfree water is constant in amount, is not in accordance with the experimental data of the freezing-point determinations. This has led Bouyoucos to an experimental examination of unfree water at different moisture contents, using the dilatometer method (35). He finds that the unfree water does not vary in amount, but is a constant quantity for any given soil, whatever the total moisture content. Thus the deductions from the freezing point method do not agree with the experimental evidence of the dilatometer method, if it be assumed that the unfree water as measured by one method is identical with that measured by the other.

Bouyoucos' paper has only recently appeared, hence nothing can be done at the present moment except to record the differences between experiment and deduction. It is obvious that the whole matter is in an extraordinarily interesting position, and in view of the extended use now being made of these methods—especially the freezing point determinations—in Michigan, California, and elsewhere, it is important that the causes of the discrepancy mentioned should be examined; work in this direction has therefore been put in hand at Rothamsted.

In this discussion of the relations between the soil and its moisture content a comparison has been made between the original hypothesis and the modern one. It has been shown that the colloidal material in the soil exercises a profound effect on the moisture relations, and that these relations are continuous over a wide range of moisture content. The majority of the various subdivisions and equilibrium points which were developed on the older hypothesis are not to be regarded as having any deep physical significance, and in one or two cases their interest is physiological rather than physical.

Further progress in our knowledge of the moisture relations in soil is most likely to follow if its colloidal properties are taken into account.

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NOTE ON THE HYGROSCOPICITY OF CLAY AND THE QUANTITY OF WATER ADSORBED PER SURFACE-UNIT.

By Sven Odén.

As is well known, specimens of soil which have been exposed to the air until to all appearance quite dry, still contain a quantity of water, the so-called *hygroscopic* water. If the soil in question is of a coarse nature, as, for example, sand or silt, this amount of water is relatively small, while in the case of fine-grained clays it can amount to as much as 20 per cent. or more.

But the amount of hygroscopically-bound water is, of course, not solely dependent on the nature of the soil in question, but also on the greater or less saturation of the atmosphere with water vapour; that is, on the vapour pressure of the water in the air.

Curiously enough, there are for soils hardly any published researches on how the amount of this hygroscopic or adsorbed water (after equilibrium is reached) varies with changing pressure of water vapour in the atmosphere in which the research is conducted, while, in the domain of colloid chemistry, in the case of gels, this has shown itself to be an excellent method for characterising these in order to determine their internal structure.

I have therefore begun a research of this nature, conducted in such a way that the soil samples—up to the present they have been chiefly clays—were simply allowed to lie in a large desiccator containing a sulphuric acid-water mixture, the vapour pressure of which was taken by Regnault's[1] measurements. The weight was determined from time to time, and after about a month was found to be constant, showing that equilibrium had been attained between the adsorbed water and vapour pressure of the water in the atmosphere of the experiment. Thereupon the desiccator was filled with more concentrated acid, the clay gave off more water, and so forth.

If we plot on a curve as abscissæ the retained amounts of water (as percentage of the *dry* soil) and as ordinates the corresponding pressures of water vapour, we obtain for each clay a characteristic curve, of which some are given in Fig. 1.

It is clear that the coarser the clays are, the less water is held, and the closer the curves approach the axis of ordinates: while the stiff, strongly plastic clays give curves lying closer to the axis of abscissæ.

While the curves for nearly all clays are concave to the axis of abscissæ, it is remarkable that the curve for Egyptian Nile clay from Korashin lies almost in a straight line from 0 to 15 per cent. of water, and then gives a sharp bend.

While such *complete* curves giving the relation between adsorbed water and the vapour pressure are up to the present known only for a few kinds of soil, the amount of water retained over 10 per cent. H_2SO_4 (corresponding to about 14·4 mm. at 18°) has, under the name of "hygroscopicity," played a certain rôle in the study of soil since, according to a theory laid down by H. Rodewald,[1] the surfaces of the particles at this pressure of water vapour would be covered with a layer of water of one molecule thickness only, and E. A. Mitscherlich[2] calculated from this the total surface area of 1 gm. of the soil in question.

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[1] Regnault, *Ann. de Chim. et de Phys.* (3) **15**, 179 (1845).

It has been pointed out many times that the whole of this theory is of a highly doubtful character.[3]

It is only necessary to proceed in the opposite direction and calculate from the surface area, which Mitscherlich calculated from the hygroscopicity, the average size of the particles, to find that one comes to such impossible results as that particles in a tertiary quartz sand should have a diameter of less than 1 μ, and that a stiff clay from Java should consist of particles of the dimensions of 1 $\mu\mu$: that is, that their suspension would, in the ultramicroscope, be amicroscopic.

It is therefore of interest that one can, by my method of studying the rate of sedimentation in a clay slime, and its variations during the time of sedimentation, obtain a measure of, at least, the order of magnitude of the total surface area the particles represent on their fall through the liquid.

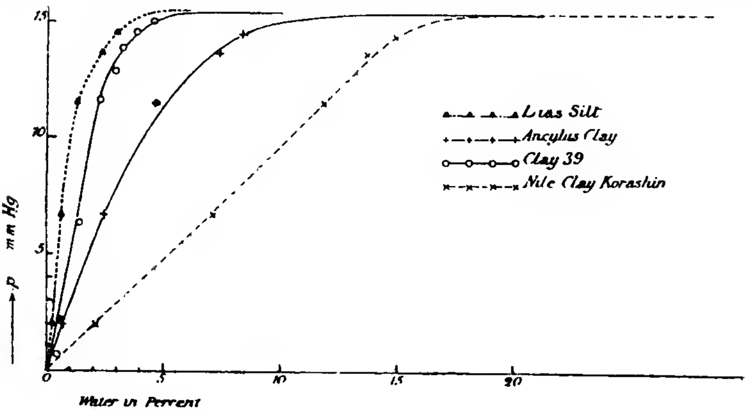

Fig: 1

If all the particles were spherical and we knew their distribution over the different ranges of size, that is, a function F(r) of such a nature that

F(r)dr gives the percentage amount in the interval r to $r + dr$

and the function N(r) is of such a nature that

N(r)dr gives the number of particles in the same interval,

we then have

$$F(r)dr = N(r)dr \, . \, \frac{4}{3}\pi r^3 \sigma, \text{ where } \sigma = \text{the specific gravity of the particles},$$

or

$$N(r) = \frac{F(r)}{\frac{4}{3}\pi r^3 \sigma} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (1)$$

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[1] Rodewald, *Zeitschr. f. Physik. Chem.*, **24**, 218 (1897); **33**, 597 (1900); *Landw. Versuchsstationen*, **59**, 434 (1904); *Landw. Jahrbücher*, **31**, 675 (1902).

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$N(r)dr$ gives the number of particles in the interval r to $r + dr$. If the interval is small we may regard the particles as of equal size and the *surface area* of each $= 4\pi r^2$.

The combined surface areas of the particles in this interval of radius become therefore

$$N(r)dr \,.\, 4\pi r^2 = \frac{F(r)}{\frac{4}{3}\pi r^3 \sigma} dr \,.\, 4\pi r^2 = \frac{3F(r)}{r\sigma} dr \quad . \quad . \quad (2)$$

Finally, if $O(r)$ is a function which gives the surface area as a function of the radius, so that

$O(r)dr =$ surface area in the interval of radius r to $r + dr$ then clearly,

$$O(r) = \frac{3F(r)}{r\sigma} \quad . \quad . \quad . \quad (3)$$

and it is possible by integration of $O(r)$ from o to ∞ to obtain the total surface area for the amount given by the distribution curve.

The experimental and theoretical methods of obtaining distribution curves from the rate of deposition have been indicated by me in another place.[1]

Here we meet, however, the difficulty that all the particles do not settle within the time of the experiment; that is, we get a distribution curve for only a part of the clay.

By tapping off this unsedimented residue and determining its mean size of particle, I have endeavoured to obtain the total area for the unsedimented portion, with a view to fixing the surface area for the whole of the clay.

It may be stated, as an example, that for the Ancylus clay in question—(the distribution curve for this clay is published in Paper III., Fig. 17)—the sedimented portion amounted to 69·1 per cent., varying from 7μ to $0{\cdot}17\mu$. The surface area of this 69·1 gm., that is, the function $\int_{0{\cdot}17}^{7} O(r)dr$ amounted to $1{\cdot}62 \,.\, 10^6$ sq. cm.

The mean size of particle in the residue was $100\mu\mu = 1{\cdot}10^{-5}$ cm. The surface area of each particle was therefore $4\pi \,.\, 10^{-10}$. sq. cm.

For calculation of the total number of particles N the following equation applies:—

$$N \,.\, \frac{4}{3}\pi(1{\cdot}10^{-5})^3\sigma = 30{\cdot}9$$

$$N = \frac{30{\cdot}9 \times 3}{4\pi\sigma} \,.\, 10^{15}$$

and the surface area of all the undeposited particles

$$= 4 \,.\, \pi \,.\, 10^{-10} \,.\, N = \frac{4\pi \,.\, 30{\cdot}9 \,.\, 3}{4\pi\sigma} \,.\, 10^5.$$

If the specific gravity σ is taken at 2·7, we obtain the result:—

for the undeposited portion	$3{\cdot}43 \,.\, 10^6$ sq. cm.
and for the deposited portion	$1{\cdot}62 \,.\, 10^6$ sq. cm.
thus for the whole 100 gm. of clay	$5{\cdot}05 \,.\, 10^6$

or 5·05 sq. m. per 1 gm.

In this way I obtained for 1 gm. of the Lias silt 1·78 sq. m. and for the clay *39*, 1·62 sq. m.

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[1] See my third paper on the "Clays as Dispersoids" and also "Koll, Zeitschr." 1917, **18**, 33 (1916), **26**, 100 (1920).

With the Nile clay disturbances unfortunately occurred in the registration so that I was not able to calculate the surface area.

If we now express the water content in gr. per sq. m., instead of in per cent. per unit weight, we arrive at the curves given in Fig. 2.

It is clearly seen that the curves do not coincide as one might expect if each surface unit absorbed the same amount of water independent of dispersity and of chemical nature.

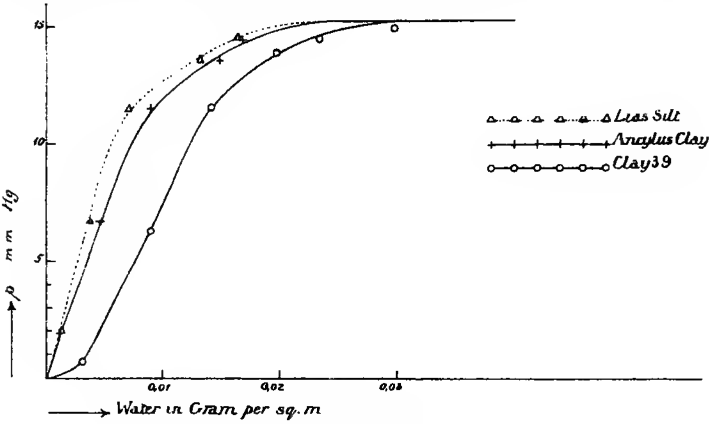

Fig: 2

Furthermore, even the sequence of the curves for water per unit surface, and those for water per unit weight, is not the same, so that a clay of higher "hygroscopicity" may have a smaller surface development than a clay of smaller hygroscopicity.

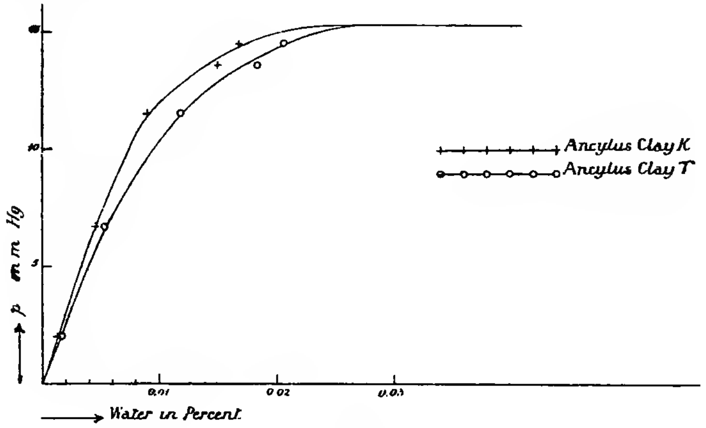

Fig: 3

It is, therefore, clear that calculation backwards from hygroscopicity to surface development of a soil is fallacious, the hygroscopicity being obviously dependent not only on surface development but also on the chemical nature and constitution of the clay.

Only when clays of closely related nature are considered, as *e.g.* layers of varying thickness and dispersity of the stratified Yoldia clay, the curves for the water retention referred to the weight and to the surface coincide as is shown by the two diagrams in Figs. 3 and 4.

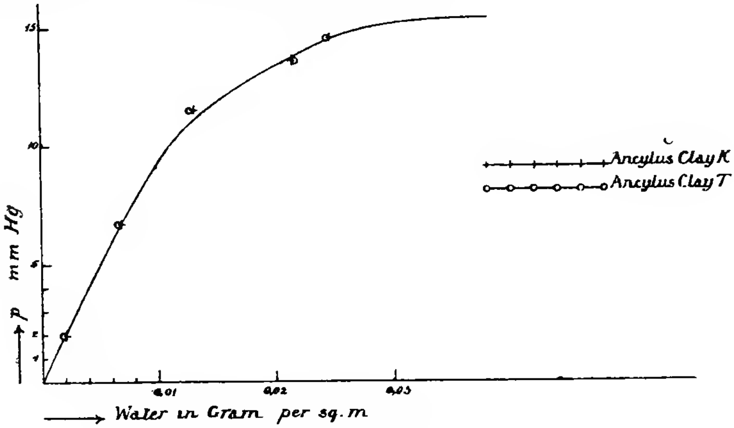

Fig: 4

Fig. 3 represents the water in per cent. by weight of two specimens with a surface development of 3·4 m^2 and 4·2 m^2 per gram weight, while Fig. 4 shows the water in grams absorbed per surface unit at varying pressures.

THE SOIL SOLUTION IN RELATION TO THE PLANT.

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(Presented by Dr. E. J. RUSSELL.)

The soil and the plant together form a multiple phase chemical system, and a more exact knowledge of the inter-relationship of the various components of this system is requisite to the advance of scientific investigations of the soil in its relation to the plant. The fertility of any soil must be measured by its ability to produce some useful crop; thus the study of soil fertility cannot be dissociated from the study of plant growth. Perhaps these ideas may be considered too obvious to require statement, yet it is true that this point of view often fails to receive proper consideration in researches dealing with soils and plants, even when the avowed purpose is that of contributing information directly or indirectly applicable to crop production.

Innumerable analyses of soils have been made to determine the total content of plant food, or to estimate what proportion of the total quantity is soluble, under arbitrarily limited conditions, in hydrochloric acid, nitric acid or other strong solvents, which at various times have been thought to bring into solution only the more or less available soil constituents. Notwithstanding the enormous mass of data obtained in this manner, no general and consistent correlation with crop production has ever been made. The conceptions of the soil which underlie this type of experimentation are essentially static in nature, while the plant and the soil form a dynamic system in which rates of processes are all-important. In this paper the writer has for his main purpose the further elaboration of the dynamic and physico-chemical viewpoint of soils and plants, first desiring to acknowledge his indebtedness to the work of the Rothamstead Station, the Michigan Station and others, and to the investigations of Burd and Stewart at the University of California.

Since the plant obtains its direct supply of mineral nutrients only from solution, the soil solution at once becomes the logical point of attack in investigations of plant nutrition. The difficulties met in researches in this field are manifold and have been overcome only to a limited degree, but certain assumptions may be made with a very great measure of confidence. Whatever may be the forces by which the film water is bound to the soil particles, it must nevertheless possess many, if not all, the chemical properties of free solutions. Among these properties certain ones may become of paramount importance to the nutrition of the plant, for example, reaction, osmotic pressure, and concentration of nutrient ions. There seems to be no valid reason against the application of physico-chemical principles applying to solutions in general to solutions which nourish the plant.

During recent years many researches have shown that the reaction or hydrogen ion concentration of solutions is of far-reaching interest to the biologist. In the realm of soil investigations there has long existed the utmost confusion concerning the question of soil reaction. Many terms have been invented to describe a varying complex of factors, such as "sour soil," "apparent acidity," "so-called acidity," "adsorption acidity," "negative acidity," etc. Numerous investigators have been loth to acknowledge that a soil solution could be acid in the same sense as any other acid solution. But we must of necessity recognise the fact that the soil solution is either acid, neutral or alkaline. The investigations of the past few years with the hydrogen electrode and special indicators seem to leave no doubt that many soils yield solutions with hydrogen ion concentrations greater than that of pure water. Such solutions are properly termed acid, and the term requires no modification.

Upon examining into the intensity of acidity (most conveniently represented by the customary pH values) of such solutions, we find that there is no evidence to prove that the acidity *per se* is sufficient to be injurious to most plants of agricultural interest, except in somewhat rare instances. This conclusion is upheld by experiments with solution cultures, which prove that plants may grow normally in solutions having intensities of acidity comparable with those found in most acid soils.[1][2] Further confirmation is afforded by observations on certain peat soils of California. In these soils many crops, including legumes, thrive and yet the acidity is of the order of pH 4·8. The so-called lime requirement of the soils is enormous, but the addition of lime has not resulted in increased crop yields.

It is, of course, undeniable that the practice of liming acid soils is most frequently beneficial to the plant, but it by no means follows that the improved environment is directly attributable to a decrease in the hydrogen ion concentration of soil solution. It has been shown that aluminum in toxic concentrations may be present in some acid soils; the decrease of acidity may be accompanied by a decreased concentration of aluminum. In other cases the base-silicate equilibrium may be of such a nature as to prevent the attainment of a concentration of calcium sufficiently great for the needs of some plants; the addition of lime may alter this system and remedy the deficiency. Many other possibilities could be suggested, including speculations concerning the effect of reaction on soil micro-organisms. Those interested only in the art of agriculture may object that it is immaterial what the mechanism may be, by which an acid soil is improved by the use of lime, but the scientific investigator will desire to segregate out the diverse factors of the complex system and assign to each one its due weight. In no other way can the true relation between soil reaction and plant growth be ascertained.

Brief mention should be made of soils with alkaline soil solutions. Here also elementary physical chemical principles assist in the interpretation of the data. Soils containing calcium carbonate are usually referred to as alkaline soils, and it is very generally maintained that most plants, especially leguminous plants, require an alkaline medium. A more careful consideration of the chemical equilibria leads to the inference that the soil solution of a soil containing calcium carbonate is not necessarily always appreciably alkaline in reaction. In such a system one must take into account the partial pressure of carbon dioxide in the gaseous phase of the system. It has been well established by the work of Russell[3] and others that the soil atmosphere may contain much larger percentages of carbon dioxide than the outer atmosphere. The real reaction of the soil solution will be dependent in part on the partial pressure of carbon dioxide. If this

[1] Hoagland, D. R. (1918), *Science*, N.S., Vol. XLVIII, pp. 1-8.
[2] *Ibid.* (1919), *Jour. Agr. Res.*, Vol. XVIII, pp. 73-117.
[3] Russell, E. J. and Appleyard, Alfred (1915), *Jour. Agr. Sci.*, Vol. VII, pp. 1-48.

partial pressure be sufficiently great a nearly neutral or possibly slightly acid reaction will be found in such soil solutions. The hydrogen ion concentration would be subject to continuous modification with fluctuations in the carbon dioxide content of the soil atmosphere. Since the plant at certain periods may bring about a large increase of carbon dioxide in this atmosphere, it is evident that the plant may exert an appreciable effect on soil reaction in soils of this character. The soil micro-organisms have a like significance in this connection.

In arid regions soils are often found in which the reaction is determined by a sodium carbonate, bicarbonate, silicate system. Under these circumstances an excessive hydroxyl ion concentration may sometimes exist, the intensity of alkalinity being sufficiently great to destroy most useful plants. In general, for a similar divergence from the neutral point, within a limited range, the hydroxyl ion seems to be more toxic than the hydrogen ion. In these soil systems also carbon dioxide is an essential factor, and its presence tends to decrease the actual alkalinity of the solution. Recent work has indicated that it is impossible to understand the effects of such soils on plants unless this factor be given consideration.

While the reaction, or hydrogen ion concentration of the soil solution is of extreme interest in many special cases, the concentration of the nutrient ions is of universal significance to soil fertility investigations. Two great obstacles have hindered progress in this field; first, the difficulty of separating the soil solution from the soil mass, and second, the fluctuating nature of the solution. Lipman[1] and others have attempted to obtain the soil solution with the use of great pressure, but definite conclusions have not been formulated at the present time. The approximate magnitudes of total concentration of solutes in the soil solution have been determined by Bouyoucos and McCool,[2] by means of an application of the method of freezing-point depression. Some of the results secured with the aid of this procedure have thrown considerable light on the whole question, although it is not at all certain that the small differences in depressions of the freezing-point noted in some investigations do not fall within the limits of experimental error. Observations from freezing-point determinations indicate that the fertile soils examined had, at optimum moisture content, solutions of concentrations represented by from ·05° C. to ·15° C. freezing-point depression, when the concentrations were at the maximum. After the depletion of the solution by the plant, the values frequently fell off to as low as ·01° C. to ·005° C., or even less.[3]

Analyses of water extracts of soils, periodically carried out, have contributed greatly to our knowledge of the solutes available to the plant. Studies on the relations existing between the freezing-point depression and the quantity of solutes dissolved in water extracts have indicated that in general the concentration of the soil solution is reflected in the extract. Still other applicable data have resulted from experiments on the equilibria between soil extracts and soil mass,[4] and these have suggested that the ratios between some of the solutes may be similar in the soil solution and in certain types of water extracts.

Incomplete as our information is we may still construct on the basis of our present knowledge an outline of some of the important characteristics of a soil solution, pertaining to its nutrient properties. It is very certain that soil solutions are of infinite diversity. The theory at one time advanced by Cameron, to the effect that all soil solutions were saturated with respect to important nutrients is of course untenable. Indeed the fallacies of this conception were long ago clearly pointed out by Russell.[1] It has required the recent work, however, to establish more definitely some of the relations existing between crop and season and the soil solution.

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[1] Lipman, Chas. B. (1918), *Univ. of Calif. Pub. Agr. Sci.*, Vol. III, pp. 131-34.

[2] Bouyoucos, G. J., and McCool, M. M. (1916), *Mich. Agr. Exp. Sta. Tech. Bul.*, 24, pp. 592-631.

[3] Stewart, G. R. (1918), *Jour. Agr. Res.*, Vol. XII, pp. 311-68.

[4] Hoagland, D. R. (1920), *Jour. Agr. Res.*, Vol. XX, pp. 381-95.

These relations can perhaps be conveniently illustrated by a brief reference to the California experiments. Large quantities of different soils were collected in one place and after very careful mixing they were placed in containers, each of about one ton capacity. Two containers of each soil were installed, one being cropped to barley and one remaining uncropped. Samples of the soils were taken every two weeks and the water extracts analysed. During the early period, while the plants were still very small, an increase was noted in the quantities of nitrate, potassium, calcium, and magnesium extracted. After the plants had begun to grow more rapidly the amounts of these elements in the extracts started to decrease, and by the time the plants were well tillered and the heading-out stage had been reached, little if any nitrate remained, and in general very significant depressions of soluble potassium, calcium, and magnesium had occurred. Meanwhile the uncropped soils failed to show these decreases in the water-soluble nutrients although marked fluctuations were found, probably associated with cycles of activity of micro-organisms. In these uncropped soils the highest point in the seasonal curve was frequently attained at the time when the cropped soils were at a minimum. The water-soluble constituents of the latter slowly increased in quantity after the periods of greatest depression, but the difference between the cropped and uncropped soils persisted for a long time, sometimes being evident at the beginning of the following season. Later other crops than barley were experimented with and very similar results were obtained.

The seasonal fluctuations which have just been described do not seem to hold for phosphate. The water-extractable phosphate on the whole is maintained at a fairly constant level throughout the season, but different soils yield very different quantities of soluble phosphate. While no marked changes are noted during a single season, after a number of years of cropping some soils show a decided depression in the solubility of phosphate. Thus we may assume that the crop does produce an effect on the concentration of phosphate ion in the soil solution, but the chemical system involved requires special consideration. The total quantity of phosphate extracted from a soil is approximately proportional to the amount of water used, which is not true of potassium, calcium, magnesium, and nitrate.

The next step in the investigation was to follow the absorption of nutrient elements by analysing the crop itself at various stages in the growth cycle. This task was undertaken by Burd,[2] and his experiments indicated very definitely that the absorption of certain elements was characterised by several distinct phases, coincident with important stages in the development of the plant. Up to the time of heading out the total quantities of all elements increased in the tops of the plants. At this period a new phase began during which a loss of nitrogen and potassium from the tops (and possibly a slight loss of calcium and magnesium) occurred. Later there was a period of renewed absorption.

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[1] Russell, E. J. (1905), *Jour. Agr. Sci.*, Vol. I, pp. 327-46.

[2] Burd, J. S. (1919), *Jour. Agr. Res.*, Vol. XVIII, pp. 51-72.

Perhaps this course of events might be thought to be inherent in the growth of the plant. When, however, plants are grown in solution cultures and provision is made to maintain more or less continuously a sufficiently high concentration of the nutrient elements, absorption may continue throughout the cycle of growth. It would seem probable therefore that both the diminution in concentration of the soil solution and changes in the internal metabolism of the plant are concerned in the phenomenon of loss of nutrient elements from the tops as a whole. These conclusions are based on experiments with barley, but there is reason to suppose that they are of more general application.

At this point in the discussion the question naturally arises, what are the characteristics of a soil solution producing maximum yields of crop? Many of the soils referred to in this paper produced very large yields of barley straw and grain. From this it must follow that the very low concentrations of the soil solution in the later stages of growth were not unfavourable to the production of a large crop. The important period of absorption of nutrients for barley occurred before the heading-out stage. These conclusions may not be valid for phosphate, since, as has been stated, this ion is probably maintained at a more nearly constant concentration in the soil solution, and, moreover, absorption of phosphate continues even during the period of loss of nitrogen and potassium. In an artificial culture solution the decrease in concentration occurring in soil solutions may be prevented. When this is done, and when the climatic conditions are suitable, a very large growth may be obtained from a single seed. Here a special and somewhat abnormal condition is produced, in which new cycles of growth succeed each other and great delay in ripening processes may be brought about. It also appears that plants grown under these conditions may acquire very high percentages of certain elements, notably nitrogen and potassium.

Having thus outlined some of the general relations of soil to plant, it may be well to consider for a moment the question of ratios between nutrient elements. Great importance has frequently been attached to the specific ratios between the salts used in preparing nutrient solutions. Certain definite proportions are claimed to be essential for optimum growth of a given plant. The writer feels that these claims are in no manner justified by the evidence adduced in their support. Very serious criticism may be made of the methods of experimentation and interpretation of data.[1] Another point of view bearing on this phase of nutrition may be gained by further reference to the soil experiments. It is obvious that terrestrial plants have generally adapted themselves to growth in the soil, their natural habitat, and it is not unreasonable to draw certain deductions with regard to the nutrient requirements of the plant from data on soils which actually produce excellent crops. There is no evidence from observations of this character that the plant is under the necessity of obtaining its nutrients from solutions with definite ratios between the solutes. On the contrary equal yields may be obtained from soils which give extracts with very different proportions between important elements. As is well known, the composition of plants with respect to ash constituents may vary greatly. Moreover, a brief inspection of the curves of seasonal fluctuations for soluble nutrients will show that the ratios between the solutes are constantly changing, since not all the elements are absorbed at equal rates, nor are they replenished in the soil solution in the same way. It is perhaps needless to state that extreme cases may occur, particularly in the so-called alkali soils, in which the balance of ions may become of importance.

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[1] Hoagland D. R. (1919), *Jour. Agr. Res.*, Vol. XVIII, pp. 73-117.

What, then, constitutes adequacy in a soil solution? According to Burd,[1] the soil extract, even of a soil of inferior production, contains at any time a sufficient quantity of water-soluble nutrients for the needs of the plant, as judged by actual absorption of these elements by crops growing in fertile soils. This apparent anomaly is capable of explanation when we take into account several important factors which limit the interpretation of data obtained by the method of water extraction. In the first place it is to be noted that at the time of greatest depletion very little nitrate remains in the soil. The analytical difficulties are of such a nature that an overestimate of the supply of nitrate may be made when only small amounts are present. Also a large quantity of nutrients not actually present in the soil solution at a given time is dissolved from the soil mass by the excess water used in making the extracts. As already pointed out by Russell,[2] diffusion is a very important matter in this connection. Availability of nutrients should properly be measured by the rate at which these are supplied to the absorbing membranes of the root system, but experiments based on water extracts can not determine availability in this sense with any degree of accuracy. Without doubt the colloidal nature of the soil and the type of plant must be taken into consideration.

For these and other reasons it may not be possible to correlate the analyses of water extracts of soils with differences in productivity, except when the magnitudes are fairly large, but one is perhaps justified in believing that the seasonal curves for aqueous extracts of soils form the most secure basis so far considered for interpreting the nutrient properties of the soil in terms of plant production. Information leading to a greater appreciation of the role of the soil solution must also be fundamental to any rational explanation of the effects of fertilisers on soils and plants.

Our thesis concerning the plant and soil as a chemical system brings us to the consideration of another phase of the whole question. The growth of the plant is dependent not only on the soil but on temperature, light, and humidity—the climatic complex. It has sometimes been said that weather has more to do with crop yield than any modification which can be made in most soils. Furthermore, the climatic complex influences the soil solution directly and indirectly. The requirements of the plant probably vary with its aerial environment, and the effect of the plant on the soil solution must likewise vary. Neither can the effects of climatic conditions on the activities of micro-organisms be neglected, since biochemical processes are of paramount importance in their influence on the soil solution.

The dynamic view-point of soils and plants leads to certain very clear suggestions for future experimentation on soils. The rates of solubility, carbon dioxide production, nitrification, absorption of solutes by different plants, etc., must receive much more attention, and plants must be grown under definitely controlled environments. This means that in certain experiments light, temperature and humidity should be subject to variation at will. The difficulties of an adequate control in soil and plant experiments are immense, but the field of research which would be opened by these refinements of experimental methods is unlimited in its opportunities. By such researches we may hope to understand to a far greater degree than heretofore the complex system of chemical reactions which determine every step in plant growth.

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[1] Burd, J. S. (1918), *Jour. Agr. Res.*, Vol. XII, pp. 297-309.

[2] Russell, E. J. (1905), *Jour. Agr. Sci.*, Vol. I, pp. 327-46.

OSMOTIC PHENOMENA.

By Charles A. Shull, the University of Kentucky, U.S.A.

(Presented by Mr. B. A. Keen.)

A thoughtful consideration of the various relationships which exist between plants and their environment, leads one to the conclusion that none is of greater importance than the relationship established with the moisture of the soil through the roots and root hair mechanism. The fundamental character of this relation is seen clearly in the facts that soil moisture is the dominant edaphic factor in the geographic distribution of vegetation, and that some of the most striking modifications in the form and structure of plants are produced by physical or physiological dryness of the environment. The deserts of the earth have a sparse vegetation not because of infertility, but from low soil moisture content. And the succulent types of plants found in xerophytic and halophytic habitats have been developed through the physiological conditions set up inside the plant, incident to low availability of water.

As has been shown recently by MacDougal and others, the course of carbohydrate metabolism is determined in certain succulents by the amount of water existing in the cells, and the probability is that most succulent plants have been modified by the osmotic conditions in their cells. Whenever the water content exceeds the critical amount, the carbohydrates form polysaccharides of low imbibitional capacity. But if the saturation deficit becomes great enough, the tendency is for the carbohydrates to go over into pentosans which are hydrophilous. In such cases, if in addition there is the production of much free acid during the carbohydrate transformations, succulence will probably result from the combination of circumstances. Thus low availability of soil moisture may fundamentally change the metabolism of the plant, and modify its whole form and structure.

Whether we consider the influence of the plant upon soil moisture, or *vice versa*, the influence of the quantity of soil moisture upon the plant, these influences must act through the same mechanism, the osmotically active membranes of the plant. Usually these are living membranes, but osmotic membranes of cellulose, and dead cells, as in seed coats, are now well known.

When dry seeds with osmotically active coats are placed in moist soil, they absorb moisture with great power, such forces as imbibition, capillarity, surface force, hydration power of colloids, and osmotic pressure from internal salts being involved. The total power of the seed to absorb water is the resultant of all these forces working together. Opposed to these internal forces are external forces which tend to prevent intake of water. The surface forces of soils, capillarity, surface tension, adhesion, cohesion of water in thin films, osmotic action of solutes, etc., are pitted against these internal forces; and water movement into or out of the seed will take place in accordance with the lack of equilibrium between the two resultant forces. It is an interesting fact that seeds will actually germinate in a soil that has a moisture content below its wilting coefficient.

As soon as the seed begins to germinate the characteristic osmotic mechanism for soil water intake is established. The view point is general that the intake of water, its transfer through the plant body, and its distribution to the living cells, are processes involving osmotic action at various places in the organism. Although some suggestions have been made assigning to the root a rather passive rôle in water intake, it seems to me a mistake to adopt the idea that the root is mainly an anchorage organ, and that water merely filters through the root under the negative pressure of atmospheric evaporation and the cohesion of water. The osmotic delivery of water by the root to the lower end of the cohesive water columns probably goes on at a rate determined by all of the physical and chemical conditions within the soil-root system, including the cohesive pull upon the root cells. And if this does not keep pace with evaporation, the deficit in the aerial portions becomes greater and greater, and the tension stronger, until breakage of the column and permanent wilting ensues.

There is reason for believing that the drying power of the atmosphere, which fluctuates greatly with changes in relative humidity, averages not far from 1000 atmospheres. And this is the tremendous force which is responsible for the disturbance of moisture equilibrium in the leaves, generating in the cell walls bounding intercellular spaces, in the protoplasm itself, and in the vacuoles of leaf cells, those imbibitional and osmotic forces which lift the water column of the transpiration stream to the tops of even the tallest plants.

The root hair itself is very well adapted to its function as an absorbing organ. As Miss Roberts has shown, the wall of the root hair is usually the outgrowth of the middle lamella of the epidermal cell. It is lined inside by a cellulose layer deposited upon it by the living protoplasm. The external layer, therefore, is largely calcium pectate, and a pectin mucilage brings it into most intimate contact with the particles of soil minerals. As this pectic material is a hydrophilous colloid, it is highly adapted to imbibe surface moisture from the particles of soil with which it is in contact. It is worth while to note in passing that the whole problem of water intake and water outgo from the plant begins and ends in imbibition, imbibition of water from the protoplasm and vacuole by the exposed cell walls in leaf interspaces, and imbibition of water from the surface of soil particles by the pectic walls of absorbing root hairs.

There are several main problems connected with the osmotic phenomena of plant life which are worthy of consideration. These are, the nature of osmotic pressure itself, the cause of semipermeability in membranes, and the cause of unilateral movement of water across the semipermeable septum. Before considering the nature of osmotic pressure, the power of the plant to adjust itself osmotically to its environment should be mentioned. It has been fully established by the work of Hill, Drabble and Drabble, and Miss Roberts that the plant increases or decreases the osmotic concentration of its cell sap *pari passu* with changes in the environment which determine the scarcity or availability of water for the plant. Miss Roberts' work is especially significant as related to soil moisture, since she made her determinations on root-hair producing cells. She found that the osmotic pressure of the root hairs is maintained a few atmospheres in excess of that of the surrounding medium. Such changes in the root cells are accompanied by corresponding changes in the osmotic mechanism more or less throughout the entire plant, so that appropriate osmotic gradients are constantly maintained. With plants growing in the soil, a similar gradient for moisture intake exists. At the wilting coefficient the soil withholds water from the plant with a force of about four atmospheres, while the usual osmotic concentration of the sap of root cells of land plants is seven or eight atmospheres. In desert regions, of course, these pressures would run much higher. Under normal field conditions, therefore, the pressure gradient in ordinary mesophytic plants should run from four to eight atmospheres, as the fluctuation of the water withholding power is from zero to four atmospheres. At the wilting coefficient the effectiveness of the intake gradient is lost because the rate of transfer of moisture from soil particle to soil particle toward the plant becomes entirely inadequate. And now, even though the plant's osmotic pressure rises rapidly, it does not succeed in securing the needed moisture, because it is trying, as it were, to draw water from a dry well. Permanent wilting must quickly ensue in most cases after the soil reaches the wilting coefficient.

The main criticism to be made of the current discussions of the nature of osmotic pressure is that they attempt to simplify too much a process that must, like other life processes, be complex. We may attribute osmotic pressure to the difference in free energy of the solvent and solution, or to the kinetic energy of the solute acting on the semipermeable membrane. It seems to me more appropriate to consider osmotic pressure a complex force, the resultant of numerous factors. The free energy of the solvent, the kinetic energy of the solute, the chemical forces of hydration, especially in more concentrated solutions, and the attraction of ions in solution for particles of water charged oppositely while passing through the differential septum, are all factors in producing osmotic pressure. In the plant this complex force is smallest in the root hairs, and progressively increases to the farthest limits of water transfer.

The most important problems in connection with osmosis centre in the nature and causes of semipermeability in membranes. The sieve theory, the various solubility theories, the surface tension theory, and the hydrone theory are all well known. Every one of them has some supporting evidence, but all of them have their limitations, and prove inadequate to account for the known facts.

Armstrong's hydrone theory has come particularly to my attention in connection with my own work. The assumptions which are made in this theory as to the character of semipermeable membranes and the salts which they exclude from passage are of such a nature that they seem to me to necessitate the fundamental likeness in behaviour of all semipermeable membranes. If only hydronated membranes can exhibit semipermeability, and if hydronated membranes exclude all hydronated or hydrolated salts, then all membranes of this kind should have identical behaviour. The variability in behaviour of the natural semipermeable membranes, then, is a challenge to the hydrone theory.

Again, it is not possible to attribute semipermeability to some particular chemical substance in the membrane, like tannin, or suberin, or cutin, etc. Many different kinds of membranes are semipermeable, and no single substance, or class of substances, is common to them all. When copper ferrocyanide and other chemical precipitates, cellulose cell walls, or suberised cellulose, gelatin tannate, celloidin, cutinised tissue, parchment paper, and living protoplasm all exhibit semipermeability, it is certain that this peculiar property does not depend on chemical composition, but must be related rather to the structure of the membrane.

There is one property which all of these membranes have in common. They are all colloidal gels. It is my opinion that any theory of semipermeability should frankly recognise this property, and be couched in the language of the physics and chemistry of colloidal matter.

Water can undoubtedly penetrate both phases of the colloidal gel; but salt molecules attempting to penetrate the membrane would probably be prevented from travelling through the disperse phase by surface tension and other surface forces on the contact surfaces between the disperse and continuous phases. If so, they would have to travel in the continuous phase.

Recently Free has proposed a theory of protoplasmic permeability based upon this conception. He assumes that protoplasm is made up as a two-phase system in which the phases differ mainly in their percentage of water content, arranged as colloidal globules dispersed in a colloidal medium. These two phases are supposed to be so related that interchange of water between the two can occur accordingly as changes in the physics or chemistry of metabolism, or of the environment, necessitate. By such changes, the colloidal globules may increase in size while the continuous phase decreases; or, *vice versa*, the globules may become smaller while the continuous phase separating them increases in thickness at their expense. Conceivably the globules might reach such a size that the continuous phase would remain as the thinnest possible films between them, or they might enlarge until the gel is reversed, the discontinuous phase becoming a continuous medium, and the former continuous phase becoming discontinuous.

Changes in permeability and semipermeability would be related to these phase interchanges. Semipermeability would exist when the continuous phase existed in such thin films that molecular diffusion through it was impossible. Adequate provision is found here for natural differences in membranes, for they could hardly have identical behaviour unless the colloidal material were identical in kind. Two different kinds of membranes could exhibit differences in reaction toward the same solution, and one would not expect to find semipermeability behaviour identical in all membranes.

It seems clear to me that we must have a theory of semipermeability that recognises the nature of the membrane as Free's theory does. Living protoplasm is an amphoteric substance with an isoelectric point; and it may react as an acid or base depending on hydrogen ion concentration. As it is played upon by various solutes, or by temperature, or light, changes in the permeability or semipermeability relations would undoubtedly occur according to the nature of the solutes, and the effects of other factors on the aggregation in the colloidal system. In non-living membranes like seed coats, the gels are much firmer, more difficult to change, and the characters more stable than in living protoplasm. But even here one might expect changes from permeability toward semipermeability, or *vice versa*, with reagents having powerful effects on colloidal aggregation. In the problem of soil-moisture intake by roots, of course, we are dealing with a very delicate protoplasmic gel.

Finally, the movement of water through the membrane offers an interesting problem. When the osmotic cell is completely surrounded by the solvent, like an enclosed sack, and if the membrane is elastic, one can think of the pressure moving the membrane outward in every direction to include more water, rather than water moving in through the membrane. It is the membrane that moves. But in the living plant osmotic and imbibition forces set up a unilateral movement which has not been satisfactorily explained. The suggestions of Pfeffer as to protoplasmic differences on opposite sides of the cell, and of differences in concentration on opposite sides of the vacuole are too well known to need discussion. Rhythmic pulsations of the osmotically active cells cannot be assumed.

A suggestion which merits attention has recently been made by Loeb. In amphoteric membranes like the protoplasm of root hairs, and of vacuolate cells generally, the opposite sides of the membrane may be oppositely charged. If they were, Loeb points out that positively charged water particles would be driven through the membrane from positive toward negative side, where they would lose their charge after completing passage. The loss of charge allows other positively charged particles to follow; and if a whole series of cells one after the other had such properties, the series would set up a unilateral current of water; in the case of roots let us assume toward the open tracheæ of the vascular system. At least this is one of the possible factors in addition to osmotic pressure gradients, and might be responsible in part for the removal of water from the cortical cells into the open tracheæ. Electric exosmose has been suggested to account for the glandular secretion of water from cells of high osmotic concentration into ducts with lower concentrations. It can just as easily be a factor in the secretion of water into the tracheæ of roots.

The plant and its whole environment may be looked upon as a system in which atmospheric evaporation is the chief disturber of moisture equilibrium. In response to this disturbance, imbibitional and osmotic forces are set up which reach back from leaves to roots through cohesive water columns. These water columns are fed from below by an active root system which delivers its water by osmotic action and possibly electric transfer of water. The water is imbibed by the hydrophile colloids of the root hairs, from the surface of contiguous soil particles, which in turn exert surface tension, surface, and capillary forces to draw moisture from particle to particle toward the plant. This disturbance finally reaches to the ground water surface, which slowly lowers as the result of this upward movement of water during periods of no precipitation, but is maintained by precipitation from the same atmosphere which, when dry, disturbs the water equilibrium.

I am fully aware that there are many points which need investigation before an entirely satisfactory picture of the osmotic phenomena of plant life can be drawn. They are very complex phenomena, perhaps much more complex even than the considerations here brought forward indicate. But with a working hypothesis such as I have briefly outlined, we should be able by appropriate investigations to throw much light on those more or less obscure regions of the problem.

THE RATE OF ASCENT OF LIQUIDS THROUGH GRANULAR MEDIA.

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INTRODUCTION.

This note records the results of some experiments made in order to test the application of the equation for the capillary ascent of liquids in such media as sands or soils. This equation is derived readily by applying the theory of viscous flow to a vertical capillary tube. It was applied by Heber Green[1] and Ampt to the ascent of water through soils but without satisfactory results.

This series of experiments was planned to eliminate some of the disturbing factors introduced by using soils. Sands of different grades were obtained by the use of sieves. Paraffin oil was substituted for water. Owing to the low surface tension of the oil, it wets the sand easily. There were therefore no anomalous effects such as occur with water owing to the difficulty with which it wets some sands. The ascent was observed in tubes of 2 cm. diameter, closed at one end with wire gauze of 200 inch mesh. The sand was poured in and the tube gently tapped a few times as in experiments with soils.

The problem of capillary flow has lately been fully discussed by Washburn,[2] Department of Ceramic Engineering, Illinois, so it is unnecessary to set forth details here. As the liquid ascends, air is forced out so that the viscosity of the air should be considered in exact equations. This effect is ignored here, also the question of slip, and of the angle of contact. We adopt the view that surface tension acts by supporting and removing part of the atmospheric pressure from the liquid beneath to an amount equal to the capillary rise H. The theory of viscous flow gives, then, for a capillary tube of radius a immersed vertically to a depth d in a liquid of viscosity η, density ρ and capillary height H, the quantity of liquid q ascending per unit time as,

$$q = \frac{g\rho}{\eta} \cdot \frac{H + d - x}{x} \cdot \frac{\pi a^4}{8} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

For a column of sand $q = AS\frac{dx}{dt}$ where A is the cross section of the tube and S is the pore space, we can write, then, for the velocity of ascent v,

$$\frac{dx}{dt} = \frac{q}{AS} = \frac{P}{S}\frac{H + d - x}{x} = C\frac{H' - x}{x} \quad . \quad . \quad . \quad (2)$$

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[1] Green and Ampt., *Journ. Agric. Sci.*, IV, May, 1911.
[2] Washburn, *Phys. Rev.*, March, 1921.

where P is the quantity termed by Green the permeability. It is convenient to replace $\frac{P}{S}$ by a single constant C. Since the above equation is analogous to Ohm's law, where $H' - x$ corresponds to the E.M.F., v to the electric current and $\frac{x}{C}$ to the resistance, C may be considered as the specific conductivity or shortly the conductivity[1] of the granular medium for any given liquid.

The relation of C to the constants of the liquid and the diameters of the sand particles can be derived from Slichter's theory of viscous flow through spherical grains. Green[2] has given the general equation of flow on this theory in a convenient form for comparison with (2). We find—

$$C = \frac{gp}{\eta} \cdot \frac{1}{96kS}\sigma^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where σ = diameter of sand grains,
S = pore space,
$k = f(S)$.

The values of k for different values of S have been calculated by Slichter and are given by Green.[2]

Experiments with Paraffin Oil.

This series of experiments demonstrates that equation (2) can be applied to the initial stages of the ascent through a granular medium. It is well-known, however, that this ascent goes on for a long time, and the quantity of liquid retained between the particles decreases with the height ascended. We can easily distinguish three conditions, wet, moist and damp. It is found that equation (2) only applies to the first stage in which the liquid rises rapidly and wets the sand. It may be called the wet stage of the ascent or briefly the rapid rise.

This is most easily illustrated by taking the integrated form of equation (2)—

$$\log_e \frac{H'}{H' - x} - \frac{x}{H'} = t\frac{C}{H'} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and using it to calculate t from the constants found by plotting the observed velocity v against x^{-1}. According to (2) we should obtain a straight line, the equation of which can be written in the form—

$$v = CH'\left[\frac{1}{x} - \frac{1}{H'}\right].$$

TABLE I.

[*Rapid rise of paraffin oil through sand of mean grade* 0·0168 *cm.*]

x cm . .	4·7	7·85	10·85	13·90	14·6	14·98	15·3
t calc. min. .	1·3	4·30	11·5	31·6	42·0	52·0	67·5
t obs. min. .	1·0	4·0	12·0	31·5	42·0	52·0	57·5

$CH' = 10·60 \qquad H' = 15·6.$

The velocity graph against the inverse of the distance ascended is linear in the early part of the ascent as required by theory. The point at which this line cuts the axis is $\frac{1}{H}$. The graph for the ascent in Table I. is given in Figure 1. It is seen that the line cuts the axis at ·064 indicating a height of 15·6 at which the ascent should cease. As it approaches this point, the velocity, however, does not diminish according to the linear law and the graph turns sharply round to a curve asymptotic to the axis. Instead of the velocity dying down to zero according to (4), a slow creep persists. This effect is also shown in Table I. at 15·3, for which the observed time is less than the calculated time.

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[1] *Cf.* Boussinesq, *C.R.*, Vol. 159, August, 1914, p. 349.
[2] Green, *Journ. Agric. Sci.*, V, October, 1912, p. 1.

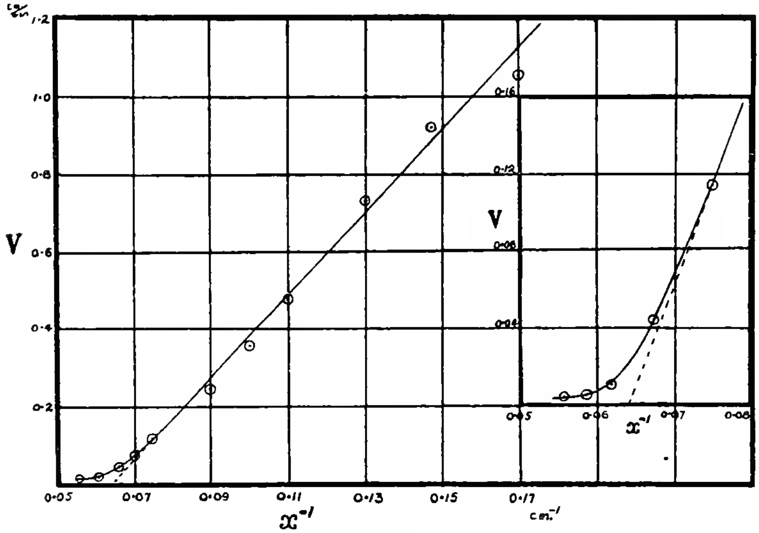

FIG. 1.

Similar results were obtained for all the different grades of sand which were examined. The values of the constants C and H determined in the above manner for each are given in Table II. and discussed below.

TABLE II.

Sand.	Apertures of Grading Sieves Cm.	Mean Grade σ Cm.	H Cm.	Hσ.	C Cm. Min.$^{-1}$.	CH^2.
River	·056 – ·028	·042	6·9	·290	2·44	115
River	·028 – ·0205	·0242	11·1	·268	·894	116
Strand	·0205 – ·0131	·0168	9·85	·165	1·57	152
			13·6	·228	·56	102
River	·0205 – ·0131	·0168	15·0	·252	·616	137
River	·0205 – ·0131	·0168	15·1	·253	·68	155
Pit	·0131 – ·0094	·0108	22·4	·242	·364	180
Moulding	·0094 – ·0076	·0085	42·0	·356	·0084	148
Mean				·257		138

The third sample in this table shows an effect which might have been anticipated, *viz.* two different rates of ascent. This would take place if the packing is not uniform or if we had a mixture of grains of markedly different grades. An initial rapid ascent through wider interstices being overtaken by an initially slower ascent through narrower spaces. We get, then, for the velocity graph two straight lines from which we can calculate the constants C and H. This set of observations has been included in this table, and treated as two independent observations on the mean grade of sand used. The mean values obtained are slightly altered, but the general conclusions are unaffected.

In this table the mean grade is taken as the mean of the apertures in the sieves used in sifting out the sand. Under H is given the capillary height of the rapid ascent deduced from the velocity graph and corrected by the depth of immersion of the tube. For capillary ascent H × radius is constant so here $H\sigma$ should be constant. Considering the material used, the relation is fairly well obeyed.

We may inquire into the possible values of $H\sigma$ with spherical grains arranged in cubical order sometimes called loose packing or in the pyramidal order of close packing. In close packing the contact of three spheres forms a curvilinear triangle. We may take the surface tension around the perimeter of this triangle as holding up a column of liquid of height H occupying the area. The result of this calculation is given below. We can make a similar calculation for cubical packing. Keen[1] applies the same mode of calculation to a column having as section an equilateral triangle. He takes Slichter's result that the pores in the sand can be regarded as of triangular section where the side of triangle $= 1{\cdot}4\ \sigma$ and finds $H\sigma = 19{\cdot}8\,\frac{T}{g\rho}$. Taking $T_{20} = 25{\cdot}7$, $\rho_{20} = 0{\cdot}799$ for the paraffin oil used, the mean value of $H\sigma$ in Table II. gives $H\sigma = 7{\cdot}84\,\frac{T}{g\rho}$. We find, then—

$$Hd = 4\frac{T}{g\rho} \text{ capillary tube of diameter } d.$$

$$H\sigma = 7{\cdot}84\frac{T}{g\rho} \text{ sand experiments.}$$

$$H\sigma = 14{\cdot}6\frac{T}{g\rho} \text{ cubical packing.}$$

$$H\sigma = 19{\cdot}8\frac{T}{g\rho} \text{ Keen's estimate.}$$

$$H\sigma = 39{\cdot}0\frac{T}{g\rho} \text{ close packing.}$$

The mathematical calculation is of course an upper limit. It assumes that at the surface the grains are all immersed to their diametral plane whereas the immersion may vary from complete immersion to mere contact. This would make a considerable reduction in the numerical constant which would account for the low value found in these sand experiments.

Since C from equation (3) varies as σ^2 we expect to find CH^2 constant. The relation is tested in the last column. The variations in the values are not excessive. From the mean values of CH^2 and $H\sigma$ we can derive an expression for C in the form of (3), $\rho_{20} = 0{\cdot}799$ and $\eta_{20} = {\cdot}0146$ for the paraffin oil used. We find

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[1] Keen, *Journ. Agric. Sci.*, IX, October, 1919, p. 396.

$$C = \frac{CH^2}{(H\sigma)^2}\sigma^2 = 2089\sigma^2 = \frac{g\rho}{\eta}\cdot\frac{\sigma^2}{25{\cdot}7}$$

or in cm. sec^{-1} units.

$$C = \frac{g\rho}{\eta}\cdot\frac{\sigma^2}{1542}.$$

The porosity of the sand in these tubes was not determined *in situ*. The porosity of a sample settled by tapping was found to be 41 per cent. In Green's experiments 39 per cent. was the usual value. We may calculate the value of C taking S = 40 per cent. and $k = 20{\cdot}3$ in equation (3). We find

$$C = \frac{g\rho}{\eta}\cdot\frac{\sigma^2}{780}.$$

The conductivity is therefore about half that given by Slichter's formula which, as Green has shown, was found in agreement with percolation experiments on sand. In such experiments the advance of the liquid is uniform, but in the capillary rise, the advance of the liquid may take place in some channels rather than others. The liquid rising in these will fill the spaces in the sand surrounding them at any level, and so reduce the rate of advance and give a smaller value for the conductivity.

INITIAL RISE WITH FLEUSS OIL.

Experiments with Fleuss oil were more difficult owing to the slow rate of ascent which spread the period of the initial rise over twenty-four hours. A full series was not completed, but enough data were obtained to confirm the conclusions stated above.

TABLE III.

Sand.	Apertures of Grading Sieves Cm.	Mean Grade σ Cm.	H Cm.	$H\sigma$ Cm.	C Cm. Min.$^{-1}$.	CH^2.
River . .	·056 – ·028	·042	4	·168	·318	5·1
			6·35	·276	·102	4·0
			(9·65)	(·405)	(·0103)	(0·94)
Strand .	·028 – ·0205	·0242	13·0	·315	·037	6·25
River . .	·0205 – ·0131	·0168	13·6	·23	·0405	7·5
Moulding .	·0094 – ·0076	·0085	38·2	·326	·00407	6·86
Mean				·263		5·94

The first example of this series also shows three different rates of ascent, which may be accounted for by the same reasons as given under Table II. It seems well to omit the third member of this set as not comparable with the rest. The observations for the strand sand seem to belong more to the next grade. For purposes of comparison the same method of averaging is again adopted. Using the values $T_{20} = 28{\cdot}6$ dynes/cm. $\rho_{20} = 0{\cdot}872$ and $\eta_{20} = 0{\cdot}242$ c.g.s. units, we find, calculating as before,

$$\left.\begin{aligned} H\sigma &= 7{\cdot}86\frac{T}{\rho g} \\ C &= \frac{\rho g}{\eta}\cdot\frac{\sigma^2}{2470}\ \text{cm. sec.}^{-1} \end{aligned}\right\}\text{Fleuss oil.}$$

in comparison with

$$\left.\begin{aligned} H\sigma &= 7{\cdot}84\frac{T}{\rho g} \\ C &= \frac{\rho g}{\eta}\cdot\frac{\sigma^2}{1542}\text{ cm. sec.}^{-1} \end{aligned}\right\}\text{Paraffin oil.}$$

Since the values of $\frac{T}{\rho}$ for paraffin oil and Fleuss oil may be taken as 32·2 and 32·8 respectively, the capillary heights for the same grade of sand for these two liquids should be equal. This is not shown in the tables, but the mean values agree in the numerical constant they give in the general formula —probably an accidental result. As regards conductivity, the ratio of the values of $\frac{\eta}{\rho}$ for the two oils is 15·2. A mean value for CH^2 of 9·08 would be expected instead of 5·95. Slight differences in packing would account for some, at any rate, of these divergencies from theoretical anticipations.

The essential conclusions remain unaltered in spite of these discrepancies in the results. We may therefore state that the initial rate of ascent of liquids in sand agrees very closely with the theory of capillary flow in tube-like spaces between the particles. As a first approximation we may take

$$H\sigma = 8\frac{T}{g\rho}$$

for the capillary rise in sand of average diameter σ, and write for the average conductivity the mean of the values given above :—

$$C = \frac{\rho g}{\eta}\cdot\frac{\sigma^2}{1900}.$$

SLOW RISE.

The slow rise which makes its appearance after the rapid rise has been completed is also in some respects similar to an ascent in a cylindrical tube. We assume tentatively that it is probably due to the irregularities in the sand grains which form passages of smaller area. The velocity graph against the inverse of the height is no longer linear. It becomes linear over a short section, however, if the ascent is reckoned from the height attained in the previous rapid rise. This is what would occur if the ascent took place in a fine capillary pore, giving a capillary height h_s, branching off from some of the main pores at their capillary height H. Using dashed letters to indicate heights measured from the bottom of the tube instead of the liquid level, the velocity equation becomes—

$$V = C\frac{(h_s' - H') - (x - H')}{x - H'} = C(h_s' - H')\left[\frac{1}{x - H'} - \frac{1}{h_s' - H'}\right].$$

Having determined C and $h_s' - H'$ from the linear portion of the graph we can use equation (4) to calculate the time substituting $x - H'$ for x, $h_s' - H'$ for H'. To this value of the time has to be added the time T taken to reach H since the ascent only begins from this point. The results for the same tube as in Table II. are shown in Tables IV. and V.

TABLE IV.

[*First slow rise of paraffin oil in sand of grade* ·0168 *cm.*]

x in cm. . .	16·5	17·4	18·3	19·2	21·1	22·0	22·9	23·8
t calc. in hr. . .	2·36	4·9	9·50	17·0	45·2	71·0	113·0	197
t obs. in hr. . .	2·50	5·0	9·65	16·6	46·2	71·5	106·8	167

$h_s' = 24{\cdot}7$ $H' = 15{\cdot}6$ $C = 1{\cdot}1 \times 10^{-3}$ $T = 100$ min.

The agreement is as satisfactory as can be expected. The correction of the time zero (T) approximates to the time required by the rapid rise to reach 15·6. If the rise is due to the pull of a capillary height h_s, the conductivity is of quite a different order to that of the rapid rise in sand of finer grain having the same capillary height since $Ch_s^2 = 0{\cdot}645$.

The slow rise continues beyond this point and a second stage makes its appearance. The velocity graph plotted in the same way v against $(x - 15{\cdot}6)^{-1}$ can again be represented over a stretch by a straight line. As before the constants of this straight line can be used to calculate the time as shown in Table V.

TABLE V.

[*Second slow rise of paraffin oil in sand of grade* ·0168 *cm.*]

x in cm. . . .	23·9	26·7	29·5	32·3	35·1	37·0	37·8
t calc. days . .	8·1	16·05	27·8	45·5	72·1	101·5	117·0
t obs. days . .	5·7	16·05	31·4	50·0	75·6	97·5	110·0

$h_s' = 43{\cdot}4$ $H' = 15{\cdot}6$ $C = 1{\cdot}33 \times 10^{-4}$

It is scarcely necessary to point out the many sources of error in these observations which extend over many months during which the temperature ranged from 10° C. to 20° C. In addition we have the variations due to packing and changes of packing produced by the capillary pull causing breaks in the column of sand. The calculated values in Table V., therefore, do not show as good agreement as previous tables, but still they follow the rate of ascent sufficiently closely for a period of three months.

The results of this investigation are collected below in the few cases in which it was carried out. In all cases, the constants given here were tested by agreement between the calculated and observed times to the same degree of approximation as shown in Tables IV. and V. In Table VI., h_s of course represents the height at which each type of slow rise ceases, measured from the liquid level, while H is the capillary height of the rapid rise.

TABLE VI.

[*Summary of results on slow rise.*]

Sand.	Liquid.	Grade Cm.	H.	h_s.	$C \times 10^4$.	Ch_s^2.
River . .	Paraffin oil	·0168	15·1	24·2 42·9	11·0 1·33	·645 ·244
Strand . .	,,	·0168	13·6	23·7 41·1	4·72 0·864	·266 ·146
River . .	Fleuss oil	·0168	13·6	18·75 21·65	4·1 1·19	·144 ·056
Strand . .	,,	·0168	13·0	16·0	1·3	·033

The product Ch_s^2 is taken here again by analogy to test the theory that this slow rise is through minute channels. The observations in Table VI. extended over three months. For comparison the observations were continued over a year. In six months the heights h_s, deduced from observations over three months, were attained as shown in Table VII.

TABLE VII.

Sand.	Oil.	h_s.	Height of Ascent Cm.	
			6 Mths.	12 Mths.
River . . .	Paraffin	24·2, 42·9	41·7	50·4
Strand . . .	,,	23·7, 41·1	36·1	42·5
River . . .	Fleuss	18·75, 21·65	23·2	—
Strand . . .	,,	16·0, —	19·0	26·25

There does not seem to be any reason to consider this very slow creep which can scarcely be said to moisten the sand as a different physical process from the slow rise. It merely confirms Table VI., showing the superior ascending qualities of paraffin oil. The theory assumed that the ascent took place through fine capillaries. The results of the analysis do not confirm this view for the following reasons: (1) the values of h_s for same grade of sand should not differ as they do since $\frac{T}{\rho}$ has nearly the same value for both oils; (2) the constant C depends on the viscosity and should vary inversely as $\frac{\eta}{\rho}$, *i.e.* as 1 to 15; the average ratio is more nearly 1 to 2: (3) the value of Ch^2 should not be very different from the values in Tables II. and III., whereas it is 400 times smaller in one case and 70 times smaller in the other. There is therefore no sound physical basis for the equation proposed. It serves a useful purpose, however, in referring the results of observations to two series of constants which express them concisely.

One explanation of these results is that we have fine capillaries blocked by small dust particles. We might also take the view that we are not dealing with a true capillary ascent but with an ascent due to the diffusion of vapour in which surface tension acts by promoting condensation in the spaces between the particles.

The greater distances ascended by paraffin would then be due to its greater vapour tension. Experiments with truly spherical grains are required to decide this question.

Summary.

The ascent of liquids in sands which takes place in two to twenty-four hours, according to the viscosity of the liquid, satisfies the laws of capillary flow for the tube-like spaces between the grains.

The ascent may continue for over a year, and the final heights attained may be two to three times the height reached in the first stage. This second stage satisfies an equation similar to that for capillary flow, but the constants deduced are not in agreement with the theory of capillary flow.

DISCUSSION ON "SOIL MOISTURE".

Dr. F. E. Hackett: If I might begin by making a few remarks on Mr. Keen's paper, I would like to raise some questions about the capillary moisture in the soil. The picture that he has put before us in the first part of the paper does not seem to me to be at all adequate from the physical point of view. I wish to speak of it from this point of view and mainly with the object of getting information. I may mention that I owe my interest in soil physics to Mr. Hallissey of the Geological Survey of Ireland, who drew my attention to this problem of the passage of water through soils. Mr. Keen has stated Briggs' point of view, *viz.*, that the capillary water is held by means of a chain of particles, and that is true enough for water descending into the soil, but I do not know whether he suggests that the ascent also takes place over the surface of the particles. If so, I do not understand how it takes place. In reference to this question I have had some observations made on the ascent of oils through graded sands. Oils were used to eliminate the irregularities due to the difficulty of water wetting some sands. The investigation shows that the initial stages of the ascent may be regarded as similar to the rise in a capillary tube and takes place in the soil-pores described by Slichter. The equation for the velocity can be expressed in the form $V = C(H - x)/x$ involving only the capillary height and a constant which may be called the conductivity depending only on the arrangement and size of the sand grains. This is, of course, a well-known form, and in this connection it is interesting to note that a great deal of the work done by soil physicists is entirely unknown in the physical world, and you find many physicists studying a subject which has been treated long ago by soil physicists. For example, Washburn, in a recent article in the *Physical Review*, seems to be unaware of the extent to which this problem has engaged their attention. In the rise through sand the initial stages of the ascent takes place very rapidly, and by plotting the velocity against the inverse of the height ascended we can determine the capillary height H. Mr. Keen has in another paper given an estimate of the height in the form of an equation

$$H . D = 19{\cdot}8\ T/gp$$

where D is the diameter of the sand grain.

Mr. Keen: The point was that H was inversely related to D.

Dr. Hackett: My experiments show satisfactory agreements in this respect, but the numerical constant was found to be much smaller and may be taken as 8. This is to be expected. The values for the conductivity were also about half that given by Slichter and other observers on the theory of flow through a granular medium. The ascent, however, continues beyond the height H but very slowly indeed. What produces this slow ascent? The first suggestion would be that it takes place as before, in a capillary pore. The liquid rises to a certain height in a wide capillary tube and then makes use of smaller capillaries branching from that point to continue the ascent. The observations at any rate fit a velocity equation based on this view, but the conductivity is much smaller than required by theory, and does not show the difference that we would expect between such liquids as Fleuss oil and paraffin oil. Of course the earlier rise shows the differences due to viscosity which for Fleuss oil is about fifteen times as great as for paraffin oil. Speaking generally, I feel that this further ascent which takes place cannot be explained by the theory of capillary tubes. Physicists have not given us very much information with regard to the rate at which a liquid travels over a surface. Experiments have shown that a liquid can spread, very rapidly over a horizontal surface, but the only suggestion that has been made is that possibly the rate of diffusion of the vapour would have to be taken into consideration. We will get then, in the upper part, in some way liquid films giving a moist effect, but in the lower part of the sand column the ascent is a regular capillary rise through the pores, filling the interstices almost completely and wetting the sand.

Mr. B. H. Wilsdon: I agree entirely with Mr. Keen as to the importance of the physical soil constants, but I feel strongly that before we can attempt to employ dynamical studies in the elucidation of soil problems we must have a much clearer understanding of the statics of the question, and in particular of the "hygroscopic coefficients" about which I feel our knowledge is far from complete. From the series of empirical equations deduced by Briggs from a large mass of experimental evidence it is a simple matter to deduce the following relation :—

$$\text{Moisture-holding capacity} = 4\cdot2 \text{ (hygroscopic coefficient)} + 21.$$

No satisfactory explanation has been put forward to account for the factor 4·2 or the constant 21. Alway, who has done probably more work on hygroscopic coefficients than any other worker, definitely states that the hygroscopic coefficient should be the same as the quantity of water which a soil will absorb when in equilibrium, not only through the vapour phase, but in actual contact with the liquid. The empirical equation states that an amount of water will be absorbed which is 4·2 times the amount absorbed from the saturated vapour.

I have recently found it possible[1] to get a quantitative relationship between the quantity of water contained in an ideal soil composed of spherical crystalline particles and the hydrostatic pressure. A similar method of attack was attempted by Trouton[2] in the case of the water held by cotton wool, but no quantitative relationship was arrived at in view of the difficulty of estimating the volumes of the drops formed at the points of contact of two fibres. The same difficulty is not met when considering the drops formed at the points of contact of two spherical particles. If in the expressions I have deduced theoretically the hydrostatic pressure is put equal to zero, a condition which will be arrived at when the two principal radii of curvature of the water drop become equal, the moisture percentage—or what is equivalent, the moisture-holding capacity of the ideal soil—works out to between 22 and 23 independently of the average diameter of the soil particles.

It remains to be seen if any explanation can be found for the factor 4·2, if the empirical relationship is to be invested with real physical significance. If it were possible to find a solute which is not adsorbed by the soil colloids it could be used as a reference substance to measure the amount of water taken up by the colloids when in equilibrium with solutions of varying osmotic pressure. For this purpose I have been experimenting with sugar solutions. The results must necessarily be inaccurate, but it may be pointed out that errors due to adsorption of sugar by the soil must tend to diminish the amount of water estimated as removed from the solution. By careful estimations of the concentration a curve was obtained which was a straight line which on extrapolation to zero concentration gave a figure for the moisture absorbed by the soil used which was about 4·7 times its hygroscopic coefficient. So far only one soil has been studied, but the work is being continued in India, as a result of which it is hoped conclusive evidence may be forthcoming. If the experiment which I have mentioned is confirmed it would indicate that there is a discontinuity in the moisture curve of a soil at the hygroscopic point which is not indicated in Mr. Keen's curves.

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[1] *Mem. Dept. Ag. India (Chem. Series)*, vol. vi., No. 3 (1921).

[2] *Proc. Roy. Soc.*, lxxvii. A (1905), p. 292.

Mr. Keen, replying to the points raised, said: With regard to Dr. Hackett's remarks on the ascent of water, it is possible that the semi-saturated zone may be due to the finer capillaries, in which the water goes up rapidly, or it may be a surface movement of the water film that Briggs has postulated, but I have not been able to make up my mind whether it is one or the other or both. I am glad to hear that other experiments are being done, because it is quite an interesting and important point. Mr. Wilsdon raised one or two points, especially with regard to the hygroscopic coefficient. I quite agree that we should look at our problems from the statical as well as the dynamical point of view. In laboratory experiments we are almost always necessarily working under statical conditions, and we must remember, when we are endeavouring to explain the behaviour of water in the field, that there the water is under dynamical conditions. I should like to know, in the experiments which Mr. Wilsdon is carrying out, whether he is using sand or soil.

Mr. Wilsdon: I am using sand.

Mr. Keen: The point which I have stressed in my paper is that the deductions of Briggs, while applicable to moist sand, cannot be applied to moist soil, without considerable modification, owing to the presence of colloidal material in the latter. This colloidal complex we assume to be present as a jelly-like coating around the particles of the soil, and it profoundly modifies a lot of the relations which are deducible from the laws of pure physics. I am much interested in the experiments on the change in concentration of sugar solutions in contact with sand and soil, as I have done experiments myself on the specific gravity of soils, using a number of different liquids for this purpose, and I have got striking differences. The experiments have only recently been started, and they are not yet in a state to discuss fully, but the evidence points to considerable volume changes in the soil when in contact with various liquids which one would associate with the colloidal portion. With regard to the experimental points on the curves given in my paper on the evaporation of water from soil, you will find it mentioned in the paper that they are omitted because they always lie exactly on a smooth curve, in which no abrupt changes of direction are present. The data for evaporation over concentrated sulphuric acid gave a curve which, although continuous, showed a fairly rapid rate of change of curvature when the water was reduced to about 3 per cent. Similar experiments were therefore performed with weaker acid, chosen so as to leave about 3 per cent. of water in the soil at the end of the experiment. The rate curves in the two cases were both fitted by the same general equation, which would hardly have been the case if there had been any special physical significance in the bend at 3 per cent. shown in the evaporation over concentrated acid.

Mr. F. Ian G. Rawlins (*communicated*): Referring to the interesting paper by Mr. Shull dealing with "Osmotic Phenomena," it may be interesting to consider briefly some hydrodynamical aspects of these questions, keeping in mind the nature of such membranes as occur in the autbor's work. For a fine tube of variable cross-section A, along which fluid of density d is flowing at a point distant s from some fixed origin, it is known that the equation of continuity is $\frac{\partial}{\partial t}(\mathrm{A} \, . \, d) + \frac{\partial}{\partial s}(\mathrm{A} \, . \, d \, . \, v) = 0$ where t is time and v is velocity. In general, suppose that this equation is soluble as an explicit function of the time. Now Washburn (*Physical Review*, March, 1921) has shown that the volume of liquid which penetrates in time t into a small capillary is proportional to $\sqrt{\mathrm{T}t/\eta}$ where T is surface-tension, and η viscosity, and gives reasons for believing that this result holds for assemblages of minute capillaries, *i.e.* for porous bodies. Equating these two expressions, t is eliminated, and we have an equation representing the relationship between distance of penetration, degree of porosity (A), surface tension, and viscosity.

Of course, it is evident that in applying an analysis of the above description to concrete problems, complete accord is unlikely to be attained, and careful scrutiny would need to be made of the "dimensions" of the quantities involved, but I venture to bring forward these abstract suggestions for what they may be worth. Lack of time makes it impossible to work up the question in greater detail.

The **Chairman**: I am afraid that the time at our disposal is very short, and we must now bring this section of the discussion to a close. We should have liked to discuss several more of the topics raised in these papers, and we certainly do want more experimental work on a question incidentally mentioned, namely, that of the possible excretion of the plant to the soil solution. That question has never yet been settled, namely, whether we can get a reverse current of some of the constituents of the plant back again into the soil.

SECTION III.—PAPERS AND DISCUSSION ON "ORGANIC CONSTITUENTS OF THE SOIL."

THE PART PLAYED BY ORGANIC MATTER IN THE SOIL SYSTEM.

By H. J. Page, B.Sc., Rothamsted Experimental Station.

Introduction.

In the course of the series of changes which are involved in the transformation of unweathered rock into a fertile soil there occurs at a certain stage—when sufficient soluble nutrient salts have been formed by weathering, and provided the climatic conditions are favourable—a change of the utmost significance: the hitherto inert lifeless mineral becomes clothed in vegetation and from that time a new constituent is added to the inorganic substrate, namely organic matter[1]—carbon compounds synthesised by the plant from the carbon dioxide of the air. Only when this change has occurred can this substrate be termed a soil. The organic matter provides a rich store of energy, making possible the existence in the soil of a most varied and complex microflora and microfauna; in other words the added organic matter transforms a sterile lifeless mineral material into a living mass. Organic matter is thus *the* characteristic and essential constituent of a soil, and as such, the study of the part it plays in the soil system is of fundamental importance.

Soils fall into two broad divisions, based on their content of organic matter. There are the mineral soils in which the organic matter constitutes only a small part of the whole soil, and there are the humus or peaty soils in which it makes up the greater part of the soil. The soil organic matter possesses special and characteristic properties not wholly shared by the other soil constituents and in a humus soil these properties are conferred in a large degree on the soil as a whole, whereas in a mineral soil they are not so much in evidence, and their share in contributing to its general properties calls for careful investigation. From the agricultural point of view, especially in this country, mineral soils predominate and it is with soils of this type that my remarks will be largely concerned; but on the other hand, a large part of the scientific work which has been carried out on soil organic matter refers to humus soils. There exists therefore some uncertainty as to the validity of applying to the interpretation of phenomena observed in mineral soils, the results of investigations referring to humus soils, and it is necessary to bear this in mind constantly in the considerations which follow later.

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[1] In the case of soils formed from secondary rocks, a small amount of organic matter is already present, derived from the bodies of the organisms deposited with the rock material, from which also the calcium carbonate and calcium phosphate of the soil are chiefly derived. This "original" organic matter cannot be distinguished or separated from the rest of the organic matter of a fertile soil, but as it cannot form more than a small part of the whole (Miller, (1)) it probably does not contribute to the effects produced by the soil organic matter to any great degree.

THE NATURE AND PROPERTIES OF THE ORGANIC MATTER OF THE SOIL.

Before we can profitably discuss in detail the part played by organic matter in the soil system it is necessary briefly to review our present knowledge of the nature of that organic matter. Unfortunately such knowledge is still very meagre. The soil organic matter is derived from a great variety of different materials, consisting of crop residues (roots and stubble of cereal and other crops, leaves of root crops, etc.); straw together with animal excreta in a fairly fresh or a well-rotted condition, in the form of farmyard or stable manure; and various other organic substances largely of vegetable, but sometimes of animal origin. The soil is thus liable to receive any of the hosts of different substances which go to make up living organisms or their excreta. In practice this means that the greater part of the organic matter which finds its way into the soil consists of carbohydrates (especially cellulose) and of protein, with smaller amounts of fats, waxes, nucleic acids, and the simpler soluble bodies present in tissue fluids and in urine.

Once these substances are in the soil, a new and complex series of changes sets in, under the combined influence of chemical, enzymic, and biological agencies.[1] Most of the micro-organisms in the soil are heterotrophic, depending on preformed organic matter for their sustenance, and they effect far reaching changes in the organic matter added to the soil. But our knowledge of the metabolism of the soil organisms is most scanty, and we cannot do more than state the bare outlines of the changes which occur. Moreover, the purely chemical processes operative on soil organic matter are even less understood, masked as they are by biological processes, and in many cases we are ignorant whether certain changes are chemical or biological in character.

Broadly speaking, the organic substances present in soil may be divided into three classes:—

(1) Comparatively well-defined complex bodies of known origin.
(2) Definitely characterised simple substances.
(3) Ill-defined bodies of uncertain origin.

The first class includes the carbohydrates and proteins forming the bulk of the organic material added to the soil, and although exact knowledge of the constitution and nature of these substances is still lacking, they have been widely studied and their composition and properties considerably elucidated. However, few of the substances in this class persist long in the soil in their original form. The proteins are rapidly attacked[2] and broken down to amino-acids and polypeptides, which are then built up, together with the scarcely less rapidly attacked carbohydrates, into the tissues of the soil organisms. Cellulose, the predominant carbohydrate in vegetable tissues, is not so rapidly attacked as the starch, gums, and sugars, but ultimately it also is broken down, partly by specific celluloclastic organisms, and possibly partly by chemical processes. Certain of the minor constituents of plants, of the nature of waxes or resins, are much less liable to attack in the soil, and they may persist for a long time unaltered (see later, p. 283).

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[1] In the case of farmyard manure, these or similar changes have already taken place to some extent, depending on the time which the manure has been stored before application to the soil.

[2] With the exception of such substances as hair, hoof, and horn, of scleroprotein nature, which are more slowly broken down owing to their resistant nature.

The second class includes the simple soluble substances such as amino-acids, other organic acids, aldehydes, bases and the like, produced from substances of the first class by the processes just outlined, or present in manure added to the soil and derived largely from urine. These simple organic substances are of great importance as links in the chain of biochemical processes by which nutrient materials, particularly ammonium salts and nitrates, are produced in the soil by micro-organisms, and thus made available to the plant. This and other aspects of the direct effect of soil organic matter on plant nutrition are considered later (p. 279).

Both of these classes, however, only account for a part and usually a minor part of the total organic matter of the soil, and represent mainly " plastic " substances which have only a more or less transient existence in the soil. The rest of the soil organic matter, excluding that actually forming part of living organisms, which, as such, does not come within our purview, belongs to the third class of substances—ill-defined, complex bodies of uncertain origin and nature, which are sometimes conveniently though loosely described as " humus ". This term is still occasionally used to refer to the whole of the soil organic matter, but it is generally restricted nowadays to the class of dark coloured, brown or black amorphous bodies which are produced in soil from vegetable matter under the combined influence of air and moisture, and which are essentially a characteristic soil product.

Of the exact *origin or mode of formation of humus* we know little, beyond the fact that it is undoubtedly derived mainly from carbohydrate material.[1] Very probably micro-organisms play some part in the chain of processes connecting carbohydrates with humus, but we do not know whether the actual formation of dark coloured humus material is the result of purely chemical or of biochemical action. Humus has a less transient existence in the soil than most of the substances belonging to the other two classes considered, but nevertheless it is always slowly changing and disappearing from the soil; it is a material which must include a number of substances ranging from the first stages of its formation from carbohydrates or their colourless decomposition products, to the last stages of its decomposition into other colourless simpler substances. It is, in fact, a mixture of unknown complexity. But, as the most characteristic part of the soil organic matter, it plays an important part in soil fertility.

With regard to the *chemical characteristics of humus* all that can be said definitely is that it is a colloidal material containing carbon, hydrogen, and oxygen in proportions varying round a certain average[2] and possibly nitrogen; and that part of it is acid in character. It is its colloidal nature which, besides playing a dominating part in its effect on the soil, is responsible, together with its variable origin, for much of the uncertainty and vagueness of our knowledge of its properties and composition. Since Achard, in 1786, first described the extraction of a black substance from peat by the action of alkali (2), a large number of investigators, whose names include many of the best known workers of their time (*e.g.* 3, 4, 5, 6, 7, 8,

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[1] There is a close resemblance in properties and composition between the " humus " produced artificially by the action of acids or alkalis on reducing sugars, and natural humus; although many workers have assumed the identity of these two products, this is far from established, although there is little doubt that they are closely related.

[2] The composition of humus is roughly: carbon 57 to 66 per cent., hydrogen 4·3 to 5·4 per cent. and the remainder oxygen, reckoned on an ash-free and nitrogen-free basis.

9, 14), have isolated from humus soils and from mineral soils, preparations which have been given definite names such as humin, ulmin, and humic, ulmic, crenic, apocrenic and geic acids, and frequently these have been analysed and assigned definite chemical formulas, although criteria of their purity and homogeneity did not exist. Scarcely any two preparations agreed in their composition or their detailed properties, though they were all of general similarity, and only in recent years, after the essentially colloidal nature of humus was demonstrated by van Bemmelen (10), and when special methods had been elaborated for dealing with colloidal substances, has any real progress been made. One of the foremost of recent workers on humus is Prof. Sven Odén (11, 12, 13, 16), whom we shall have the pleasure of hearing shortly, when he will give an account of part of his work on this subject.

The term *humus,* in its strictest chemical sense, is now applied only to that part of the dark organic colloid which can be extracted by the action of dilute alkalis and reprecipitated by acidification, while that part which is not dissolved by alkali is known as *humin.* About this insoluble humin we know very little, especially for mineral soils, for there is at present no means of separating it from the large excess of mineral matter, and although the humin of humus soils is not always so contaminated, it cannot be fractionated or purified to any extent. Brown water-soluble acid substances are also present in the alkaline extract; these remain in solution after the humus has been precipitated. Odén has proposed the name of *fulvic* acids for this class of bodies. The alkali-soluble humus can be fractionated by the use of alcohol, which removes a substance that was given by Hoppe-Seyler (14) the awkward name of *hymatomelanic acid,* while the residue insoluble in alcohol is known as *humic acid.*

It is this *humic acid,* or its more impure form before alcohol extraction,[1] which has received more attention than any other separate fraction of the organic soil colloid, although the insoluble humin may often quantitatively exceed it. Many of the deductions which may be drawn from the properties of this humic acid, or its salts, in seeking to explain the known effects of organic matter in the soil, must therefore be accepted with caution (*cf.* 15).

Odén has shown that humic acid gives true salts with alkalis, and that solutions of these salts can be freed from neutral colloids, and possess a true electrolytic conductivity (11, 12, 16). That is to say, the term humic acid is chemically correct; it is a true acid or a mixture of true acids, giving humate ions; by conductivity and potentiometric titrations, and other means, he was able to determine the equivalent of the acid, which he found to be of the order of 350, and to show that it was probably tri- or tetra-basic. I will not enter into this in more detail as Prof. Odén will himself describe this work in the next paper.

Although the soluble alkali salts of humic acid give true solutions, the free acid, and its salts with other metals, are insoluble colloids. Humic acid is thus allied to the class of colloidal electrolytes which Bayliss, Donnan, and especially MacBain, have investigated (17, 18, 19, 20), and many interesting problems on the properties of the solutions of alkali humates as compared with the soaps, and such dyestuffs as congo red, are opened up, some of which are being investigated at Rothamsted.

Although, as a result of this recent work, our conception of humic acid has become a little clearer and more definite, it must still be regarded as a mixture of allied substances, rather than as a single chemical individual. A further step in the fractionation of humic acid has recently been made by Beckley (21) who separated it into two fractions, one soluble and one insoluble, by the action of pyridine. Further work on the fractionation of humic acid is in progress at Rothamsted at the present time. The physico-chemical methods elaborated by Odén will provide most valuable criteria, hitherto almost entirely lacking, whereby the fractionation of humic acid, and the properties of the fractions may be followed and controlled. This work is the more important since it refers to the humic acid of mineral soils, for most of the recent work, including that of Odén, refers to the product from humus (peat) soils, and although the humus of mineral soils probably closely resembles that of peat, it is by no means certain that the two are identical. With regard to the relation of humic acid to humin, it is probable that the latter is an anhydride of the former. Humic, hymatomelanic, and fulvic acids are also apparently interconvertible and presumably represent, with humin, successive stages in the breakdown of the latter in the soil.

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[1] It is practically only since 1912, when Odén's first paper on humic acid was published (11) that this name has been restricted to the alcohol-treated substance. Prior to that date humic acid usually meant a mixture of humic and hymatomelanic acids at least.

Enough has been said to demonstrate the uncertain state of our knowledge as to the chemical nature of humic acid and humus in general. This is not the occasion to discuss that side of the matter further, beyond pointing out that owing to the colloidal and strongly absorptive nature of humus, we are still uncertain whether the nitrogen it contains as usually isolated is an essential part of it, as maintained by Maillard (22), or only present in the absorbed state, the pure acid being nitrogen free, as believed by Detmer (8) and by Odén (13, p. 175).

It is the *colloidal nature of humus and humic acid* and its insoluble salts which is of the greatest importance in relation to the part played by humus in the soil system. That humus is a colloid was first recognised by van Bemmelen (10), and its colloidal properties were studied by him in connection with his remarkable work on the absorptive properties of soils. He showed that the absorption phenomena displayed by humus were quite analogous to those shown by inorganic gels such as those of the dioxides of silicon, tin, or manganese. Since van Bemmelen's time, the colloidal nature of humus has been investigated by several workers (esp. 23, 24, 25).

Humin is not capable of sol formation, but humic acid is readily dispersible. It behaves as an emulsoid; its hydrosols are relatively insensitive to flocculation by electrolytes. The frequent occurrence of sols of humus in nature, in waters coming from peaty districts, is partly due to this fact, especially where polyvalent (*e.g.* Ca) ions are scarce. Humic acid sols can, however, be flocculated by electrolytes if these are sufficiently concentrated, especially by polyvalent cations such as those of calcium or heavy metals. Salt formation may be partly concerned in this. W. Thaer (26) found that this flocculation again ceases above a second limiting value of electrolyte concentration. This is a very interesting example of an upper and lower limiting zone for flocculation by electrolytes, a phenomenon usually only observed in the mutual precipitation of two colloids, but it requires confirmation before it can be taken as definitely established. Humic acid sol is also flocculated by other colloids such as tannin, ferric hydroxide, etc. Freezing causes flocculation of humus sols and this flocculation may under certain circumstances be irreversible. The particles of humus sol are very small; according to Odén they are amicrons of an average diameter of 20 $\mu\mu$. The conductivity of such sols was found by Baumann and Gully to be of the same order as that of a gold sol (see also Odén, 13). Like silicic acid, humic acid is an electronegative colloid (26, cf. Sprengel, 4) but the charge can be reversed by certain electrolytes. In alcohol the particles appear normally to carry a positive charge, but this again is not certain. Some humus sols are also stated to be diffusible through semi-permeable membranes. This would not be entirely unlikely if the particles were of amicroscopic size, and might have an important bearing on questions of plant nutrition. There is, however, considerable doubt attaching to the validity of this (cf. Odén, 13, p. 135) and of several of the other quoted observations of the properties of humus sols, owing to the uncertainty existing as to the purity and homogeneity of the material studied. Contamination with alkaline humates or with fulvic acids, which is more than probable for some of the preparations used, would account for many of the phenomena observed.

As an emulsoid, humic acid possesses protective properties. This is illustrated by its use by Ehrenberg and Pick (27) in the preparation of gold sol. The protective action and, on the other hand, the mutually flocculating action of humus and other colloids, especially clay, is dealt with in more detail later (see p. 280).

With regard to humus gel, little is known with certainty. It swells very considerably in water. Wollny (28) obtained the following values with peat:—

	Increase in Volume on Moistening, Per Cent. of Dry Volume.
Peat extracted with hydrochloric acid and ether	15·9
Natural peat from Donaumoor, 0-0·2 m. depth	46·8
,, ,, ,, ,, 0·2-0·4 m. ,,	50·2
,, ,, ,, ,, 0·5-0·8 m. ,,	60·1
,, ,, ,, ,, 0·8-1·1 m. ,,	83·8

It will be noticed that the greatest swelling is obtained with peat from the deeper and more humified layers.

Zailer and Wilk (29) similarly record the absorption of 61·8 and 77·8 per cent. of water in 3½ and 7 days respectively by dried peat kept in a moist atmosphere. This swelling may be so violent that a completely dried humus gel may undergo violent decrepitation on wetting (30). The swelling of humus gel is considerably enhanced by hydroxyl ions, especially in the absence of polyvalent cations. The water in swollen humus gel is only expressed with the greatest difficulty except in the presence of flocculating agents, which greatly assist the expression of water. This question is of great practical importance in connection with the utilisation of peat. Many patents have been taken out for processes designed to facilitate the de-watering of peat (*cf.* Nitrogen Products Committee, Final Report, p. 302 *et seq.*, H.M. Stationery Office, 1920). The effect of this swelling of humus gel on the physical properties of soils is considered in more detail later (pp. 281 *et seq.*).

The reverse effect, that of shrinkage on drying, is very marked with humus. Peat soils are notoriously liable to violent shrinkage on drying, the dried material having in some cases less than one-tenth of its wet bulk. The change is not entirely reversible, for dried humus does not usually regain its former volume on re-wetting.

The *absorptive power of humus* has been more studied, and has given rise to more controversy, than almost any other of its properties. This property of humus plays a most important part in the soil system, especially in regulating the supply of soluble nutrient materials to the plant roots. Humus is especially active in absorbing bases, but in the light of recent work in which the truly acid character of the humic acid fraction of humus has been demonstrated, it is certain that a part of this action is purely chemical. There is, however, little doubt that surface action also occurs to a considerable extent. The alleged selective absorptive power of humus for cations, and the phenomenon of absorption with basic exchange, have been greatly disputed points in connection with the question of soil acidity, and will be referred to again later.

Having thus reviewed the existing state of knowledge as to the general nature and properties of the organic matter of the soil, we now pass on to consider in detail the part which that organic matter plays in the soil in virtue of those properties.

THE RÔLE OF ORGANIC MATTER IN THE SOIL.

The beneficial effects of organic matter in the soil are well known to the agriculturist, and this knowledge is reflected in the fact that in any sound system of husbandry, steps are taken to maintain the amount of organic matter in the soil at a sufficiently high level by dressings of dung, or the application of green manures, at suitable intervals. Two examples will serve to illustrate the practical importance of organic matter. On the mangold field (Barnfield) at Rothamsted, the soil on the plots receiving only artificial manures gets into such a bad physical condition, sticky and unworkable, that under bad weather conditions the young plant grows only with difficulty, whereas on the plots receiving dung annually the soil is always in good heart, and the young plant does well, although the actual amount of plant food in the soil is the same in both cases.

In the classical wheat experiments (Broadbalk field) the dunged plot can always be relied upon to give a good crop of wheat, withstanding adverse conditions well, and fluctuating much less from year to year than the crops on adjoining plots which receive only artificial manures.

In attempting to explain the way in which the organic matter plays its part in the soil, we must first try to get some idea as to its *distribution and state in the soil mass.* The modern view by which the soil is regarded as a mineral framework, the particles of which are coated with a colloidal jelly-like layer, containing the soil solution, has been discussed in the previous section of this general discussion. The humus colloid must be regarded as constituting a large part of this jelly-like layer. The idea of such colloidal films on soil particles is by no means new. Senft (31) evidently imagined such layers,[1] and showed that humus is absorbed by sand; Schlösing père (32) assumed that the soil particles absorbed humus on their surface. He found that the proportion of organic matter[2] in the different mechanical fractions of soil increased as the size of the particles decreased, that is, as the specific surface increased. The absorptive action of sand on humus was studied in detail later by Dumont (33). It is a well-known fact that as soon as the proportion of organic matter in a soil approaches about one-fifth of the total, the properties of that organic matter are dominant in the soil as a whole and differences due to the mineral constituents are masked.

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[1] His words are: "Kommt nämlich solch feinzertheilter Humus mit wässerigem Thonschlamme in innige Berührung, so saugen sich beide Körper gegenseitig so fest an einander an, dass auf jedes Thontheilchen irgend ein Quantum Humus kommt. . . ."

[2] Measured by the loss on ignition.

With regard to the chemical state of the humus colloid in normal mineral soils, the humic acid fraction must be regarded as existing in the form of its salts with alkaline earths, particularly calcium, for most fertile mineral soils contain an excess of "lime". The neutral colloid, humin, and the insoluble humates are also of course more or less saturated by absorption of various salts and simple substances.

The effect of organic matter on the soil may be broadly classified as direct and indirect with regard to the relation of the soil to the plant. The *direct effects* do not much concern us on this occasion. They may be either directly nutritional or they may have a growth-promoting (accessory) or toxic action. In the old days humus was regarded as the prime food of plants, and in the first half of the nineteenth century controversy raged around this point. Davy and Berzelius were among those who still supported the humus theory of plant nutrition, which was, however, disproved by the work of de Saussure, Senebier, Boussingault, and especially by Liebig in his famous British Association address in 1840. The humus theory in a more restricted form was revived later by Grandeau, but found little acceptance outside France; at the present time, although there is no doubt that plants can flourish with no supply of carbon other than the carbon dioxide of the air, there is increasing, though not yet decisive evidence, that the absorption of nutritive organic substances by the roots may occur under certain circumstances. The possibility of the presence in soil of growth-promoting, accessory substances was brought into prominence by the work of Bottomley, but the question is still an open one. With regard to the presence of toxic organic substances in mineral soils, this has been established beyond any doubt for some American soils, but similar investigations for British soils have not been made. The work of Pickering on the root influence of one plant on another makes the presence of toxic substances in soils carrying a growing crop very likely, but these must differ entirely from those isolated by American workers, and can have only a transient existence in the soil.

It is in the *indirect effects* of organic matter on soil fertility that physical and physico-chemical problems are most in evidence, and in considering these effects they will be treated under four main heads, with regard to their bearing on soil texture, soil moisture, soil temperature, and soil solution.

The *influence of organic matter on soil texture*, or tilth, is of paramount importance. The object of all cultivation operations is to get the soil into a workable, crumbly condition, forming a good seed bed and keeping the soil sufficiently open for a good supply of air to the roots, and for adequate drainage. The combined action of organic colloid and calcium carbonate helps to bring this condition about in a heavy soil, where the controlling factor is the physical state of the other important soil colloid, the clay. The problem on a light sandy soil is somewhat different. There the soil texture is already too loose, and without a sufficient supply of organic colloid the soil lacks "body". It blows about in the wind, and is liable to excessive drainage and evaporation. Here again the combined presence of organic matter and calcium carbonate remedies these defects in a large measure.

In this connection the effect of colloidal humus must be carefully distinguished from that of undecomposed plant residues still possessing an organised structure. The effect of material of this type, such as unrotted straw, other plant stems and roots, is purely a mechanical one as far as tilth is concerned. Such long fibrous material opens up the soil very markedly, and greatly facilitates drainage and aeration, both in its undecomposed state, and by leaving channels after it has rotted. This action, while purely beneficial on a heavy soil, may be definitely harmful on a light sandy soil which is already too open in texture. For this reason, "long" unrotted manure is mostly applied to heavy land, and in any case, in the autumn, so that there is plenty of time for it to be broken down into amorphous colloid before the spring, while for light sands, "short" well rotted manure, where the structure of the vegetable matter has been largely or entirely lost, is applied in the spring, at a time when the beneficial effect of the colloidal matter is most needed.

The explanation of the action of organic matter on tilth is to be sought in the relation of the humus colloid to the soil particles. As regards the relatively coarse, sandy particles in the soil, reference has already been made to the work of Schlösing père, Dumont and others, and there is no doubt that for these coarser particles the action of the organic colloid is mainly a cementing one, binding the particles into larger aggregates and giving the crumb structure so conducive to good tilth.[1] An interesting example of this binding effect of humus colloid is afforded in the metallurgical industry. Calcium humate has pronounced binding, cementing properties, as remarked first by Chevreul (cited in 32 (1902)) and demonstrated by Schlösing père (32), Hall (34), Dumont (33), and Puchner (35). To produce this cementing effect the colloid must be in the form of a gel, not merely absorbed sol, which is one reason for the need of calcium carbonate, to provide calcium ions in the soil solution in sufficient concentration to ensure flocculation of the humus colloid, as well as to form calcium humate from the humic acid fraction.

With regard to the relation between humus colloid and the finer clay particles, the above considerations similarly hold, but in addition, other phenomena occur, for we are now dealing with the mutual influence of two colloids on each other. Humus and clay are capable of mutually precipitating each other at suitable concentrations as was demonstated by van Bemmelen (10). Spangenberg (36) studied the absorption of humus from its sols by clay. But in low concentrations, humus sol has a protective effect on clay. Schlösing père (32) (1874) observed this effect, using pure colloid clay (free from coarser particles). Among later workers, Fickendey (37), Spangenberg (36), and Odén (38 and 13, p. 197), have investigated the question. According to Ehrenberg (30, p. 126), the protective effect must be regarded as taking place in two stages; first the aggregated clay particles are peptised by the humus sol. Such a peptising action has been actually observed by Spangenberg (36) (on kaolin), and is to be expected from theoretical considerations (see also Donnan (39)). This peptising effect is followed by the formation of an envelope of absorbed humus sol around the clay particles, which then behave towards flocculating agents as if they consisted entirely of humus, and require a much higher concentration of electrolyte for flocculation. This protective action of humus on clay is doubtless one reason for the observed increase in the washing down of fine particles by heavy rain, in non-calcareous soils. It is also of significance in the ceramic industry.

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[1] It is probable that slimy or mucilaginous substances produced by the action of soil organisms (*e.g.* bacteria, algæ, worms) also contribute in some measure to this cementing action. It is also not unlikely that the binding action of fungal hyphæ shares in producing this result.

The protective effect of humus on other colloids, notably ferric hydroxide, is of great importance in relation to pan formation (see p. 321).

So far from explaining the beneficial effect of humus on soil texture, however, this protective action of humus would be a disadvantage, if it were the only effect on the clay. In point of fact, this action does not occur in soils well supplied with calcium carbonate, and when the concentration of humus is higher than that at which the protective action is most marked. In these circumstances the mutual precipitation of clay and humus, referred to above, comes into play, and results in the flocculation of the clay particles in a form in which they are intimately incorporated with humus and calcium humate gel, and readily cemented together into compound particles or "crumbs". This action would be quite analogous to the known effect of different concentrations of alkali on clay suspensions. Low concentrations of alkali have a strong deflocculating action, but at higher concentrations the reverse is the case, and flocculation of clay takes place. Clay flocculated by humus should differ from clay flocculated by electrolytes as regards plasticity, owing to the separation of the clay particles by humus gel, and this is borne out by the fact that clay which has absorbed much humus is found to be less tenacious than clay flocculated by electrolytes.

Humus colloid is an important factor in the influence of climatic conditions on soil texture. First, as regards rain, the swelling of humus colloid has been referred to already (p. 273). The faintly alkaline reaction of most normal soils assists this swelling, but it is counteracted by the presence of polyvalent ions (calcium). In soils deficient in lime the presence of much moisture will cause so much swelling that the cementing action of the humus gel is greatly lessened, and the process may even proceed so far that the humus passes into the sol form and by virtue of its protective action actually facilitates deflocculation and washing down of fine particles.

Frost may cause an irreversible coagulation of humus gel (40, 26, cf. Sprengel, 4). In the presence of alkali, however, the effect is only temporary (see also Nessler (41)). The mechanical effect of the separation of ice crystals with expansion, breaks up the humus into a finely divided state and probably exposes the mineral particles by rupturing the humus envelope.

Under the influence of drying agencies (heat of sun's rays, dry atmosphere, drainage) the humus gel contracts, and if the drying is carried far enough, the change is partly irreversible.

Peat soils behave very differently from mineral soils under the combined influence of moisture, frost, and drying. In such humic soils the proportion of humus colloid is so great that the effects are exaggerated to a marked degree, especially owing to the absence of appreciable quantities of lime. The swelling of undrained peat bogs under very wet conditions sometimes has the disagreeable result of causing a flood of liquid mud over the surrounding country. Drying of peat soils, on the other hand, gives rise to such violent shrinkage that great fissures are formed, and the whole level of the soil may fall several feet.[1] This shrinkage is greatest, the older and more humified the peat. The freezing of a wet peat, causing the production of finely divided, irreversibly coagulated colloid, followed by drying out, is probably responsible for the formation of unfertile dusty peat soils ("staubhumus"). This puffing up of a peat soil by the successive action of wet, frost, and drying, also explains the very heavy rolling which peat soils need. In some cases the shrinkage on drying may cause severe mechanical damage to the roots of plants.

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[1] Erosion of the dried peat by oxidation also plays a part here.

In mineral soils the humus colloid is not usually present to a sufficient extent for the harmful effects above considered to come into play. Indeed, the "puffing up" effect of organic matter on these soils is almost invariably beneficial except in very heavily manured garden soils, when the tilth is sometimes too loose from this cause. This puffing up, to which the Germans apply the expressive term of "Bodengare"[1] or soil fermentation, was at one time supposed to be actually due to the evolution of carbonic acid by the activity of soil organisms, but this view will not bear critical examination, and it is possible to explain the effect wholly in terms of the successive influence of moisture, frost, and drying on the humus gel, in the presence of "lime," and of soil organisms to give enough carbonic and nitric acids for the maintenance of a high concentration of calcium ions in the soil solution. The autumn rains will cause the humus colloid to swell considerably, assisted by the mildly alkaline reaction of the soil solution. Freezing of this swollen gel will cause still further mechanical separation of the mineral particles of the soil, and on subsequent drying this increased pore space will not be greatly reduced. This action may be repeated several times over during the winter months with the result that when warm dry weather finally sets in, and the humus gel contracts with drying, the pore space has been much augmented and the whole soil greatly opened up and brought into the desirable loose friable state associated with the effect of organic manures. The continued presence of calcium ions will prevent the swelling process going so far as sol formation and deflocculation of the clay. In certain circumstances, where a hard frost follows close on a period of unusually wet weather, winter crops may suffer; the puffing up effect may be so great that young seedlings will have their limited root system disturbed, so that if a dry period follows, the plants suffer from lack of moisture and nutrient salts.

There is a special modification of soil texture in which organic matter plays a controlling part. I refer to the question of "pan" formation. As this forms the subject of a subsequent paper in this general discussion I will not consider it in detail here, but will merely point out that on modern views it affords an important further illustration of the protective effect of humus sol, in this case on ferric hydroxide.

The *effect of organic matter on soil moisture* is largely consequent on its effect on tilth, and some of the broader aspects of the subject have thus been indicated above. By giving a crumbly structure to a clay soil or cohesiveness and "body" to a sandy soil it promotes conditions conducive to adequate drainage and aeration on the one hand, but preventing too much leaching or evaporation on the other. As a principal constituent of the colloidal, jelly-like coating of the soil particles, it contributes to the various equilibria in the soil moisture relationships considered in the previous section of this general discussion, and these do not need further elaboration in the present connection beyond pointing out that the superior swelling power of humus colloid compared with clay makes its share in contributing to those equilibria a dominating one. On mineral soils its influence on the moisture content is almost entirely beneficial, and is well illustrated by the following figure which shows the moisture content of adjacent plots on Broadbalk Field, Rothamsted, one of which receives farmyard manure annually while the other receives no organic manure. It will be seen that the soil of the former plot contains on the average about 5 per cent. more moisture than the latter. This effect of organic matter is also well illustrated by the work of Alway and Neller (42).

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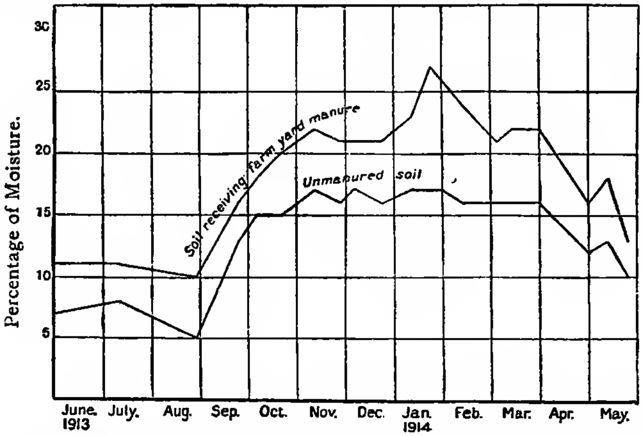
[1] There is some doubt as to the etymology of this word. It may not originally have referred to fermentation at all, but to the "making ready" (garmachen) of the soil, in its improvement by organic matter.

The effect of humus colloid in thus improving the water-holding capacity of the soil manifests itself even more strikingly in the way it holds the water near the surface and therefore available to the crop for a longer time. This is, of course, due to the inbibition of water by the gel, and also probably in some measure to the reduction in diameter of the capillary channels by the consequent swelling. Thus the tile drain under the dunged plot on Broadbalk Field, Rothamsted, does not flow except after heavy rain. This, however, does not imply that a clay soil supplied with humus is liable on that account to become waterlogged. The crumbly structure induced by a reasonable proportion of humus is still sufficient for adequate drainage, but prevents that drainage from being too rapid. It is only where the proportion of humus is so high that the soil is a peaty one, that waterlogging occurs.

On such peat soils the excessive swelling and retention of water diminish the pore space so seriously that a growing crop may suffer from lack of aeration of its roots, and from the accumulation of toxic acid products owing to restriction of the action of the beneficial aerobic micro-organisms.



[1] Fig. 1.—Curves showing the Percentage of Water in two soils on adjacent plots, one of which annually receives farmyard manure while the other does not (Broadbalk Field, Rothamsted).

The evaporation of moisture from humic acid and calcium humate gel has been studied recently by Odén (43 and 13, p. 245).

There is a curious property exhibited by some soils, which is undoubtedly largely due to the organic matter, namely, the difficulty of wetting such soils. This property is especially noticeable on some old, heavily manured garden soils, and in humus soils. It may be partly explained by the accumulation of undecomposable waxy constituents derived from plant residues but it is doubtful whether this is the sole cause, at any rate in peat soils, although some workers still ascribe it to the formation of a resinous or waxy coating on the surface of the particles of a humus soil which has been brought into a dusty, powdery state by the successive action of rain, frost, and drying (Ramann, 44, Devaux, 45). The fact that this property of peat soils is not always removed by extraction with organic solvents such as ether and alcohol, which should remove the waxy layer; and that the dusty soil can often be made to take up water by mechanical pressure, point to a possible alternative explanation of the phenomenon, where the presence of air in the fine capillaries of the dusty soil, and of absorbed air on the humus particles, which have considerable absorptive power for gases, would be the prime causes of the difficulty of wetting. Probably both these effects obtain in most circumstances, their relative influence varying in different soils.

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[1] Reproduced by permission of the University Press, Cambridge, from "A Student's Book on Soils and Manures," by Dr. E. J. Russell.

The *effect of organic matter on soil temperature* is partly an outcome of its effect on soil texture and moisture. By facilitating the production of a loose tilth on the surface and thus preventing excessive evaporation, it limits the cooling effect due to such evaporation, while by promoting adequate drainage it allows the soil to warm up more rapidly than it would if its water content were higher: the specific heat of water is about five times that of dry soil. However, humus soils and clay soils even when their humus content is high, are always moister than light sandy soils, and they therefore warm up more slowly than the latter. On the other hand, they also lose their heat more slowly in the autumn, thus prolonging the growing period.

Another consequence of the loose packing of the surface soil induced by organic matter is that the loss of heat by conduction to the lower and colder layers of soil, is reduced.

Apart from this indirect effect on soil temperature, humus exerts a direct effect; its intense brown or black colour darkens the soil as a whole and makes it more absorptive for the radiant heat of the sun, so raising its temperature. This effect is more marked on sandy than on clay soils, for the total surface of the particles being smaller in the former, an equal amount of organic matter will form a thicker coating. This enhanced absorptivity is not counteracted by equally increased radiation at night, for the dark colour does not affect the emissivity for the low frequency heat waves emitted at ordinary temperatures. The absorption spectrum of humic acid in the visible and ultra violet region has been investigated by Melin and Odén (46 and 13, p. 210).

The *effect of organic matter on the soil solution* may be discussed under two heads, with regard to the reaction of the soil solution, and with regard to its composition and concentration.

As regards the *reaction of the soil solution*, this subject is being specially treated in a subsequent paper, and therefore does not call for detailed discussion here. The old idea that soil acidity was caused by the presence of definite complex acids, such as humic and ulmic acids, has formed the subject of a long controversy in recent years, in which the school led by Baumann and Gully (23, 24, 25) ascribed the acidity of soils, at any rate as far as peat soils were concerned, entirely to selective absorption of cations by colloidal humus, and went so far as to deny the existence of any true humic acids. This was most vigorously contested by Tacke and his collaborators, and by others, and was finally shown to be untenable by Odén (11, 12, 13, 16, 47) who demonstrated, as already mentioned, that humic acid is a true acid, and his results were confirmed by Ehrenberg and Bahr (48). But he also demonstrated that although these acids actually exist, they are so insoluble that they cannot contribute appreciably to the acidity of peat soils; neither does he accept the selective absorption hypothesis, but according to his view the acidity of peat soils is due to absorbed mineral (*e.g.* phosphoric) and organic acids. So far from regarding humic acid as contributing to the acidity of peat soils, he regards its calcium salt as exerting an important buffer action in regulating the reaction of the soil by reacting with harmful soluble acids and replacing them by harmless insoluble humic acid (43). In mineral soils the same effect would be expected, and as regards the general question of the reaction of such soils, it is probable that the other effects of humus colloid on this reaction do not differ essentially from those of the other soil colloids, and therefore need not be discussed here. Kappen (49) has shown, as regards the phenomenon of absorption with basic exchange, that humus soils behave in the same way as mineral soils, thus confirming the earlier observation of van Bemmelen (10).

With regard to the *composition and concentration* of the soil solution, the organic matter produces a very definite effect. This effect depends on the absorptive power of humus, which results in the fundamentally important property of soils containing organic matter of retaining nutrient salts such as ammonium and potash salts, phosphates, etc., which are thus not appreciably washed out in the drainage water. These salts are absorbed by the humus colloid, which thus regulates the composition of the soil solution, furnishing further supplies when the plant roots absorb the salts from the solution. In extreme cases this absorption may be detrimental to the plant by actually holding back supplies of nutrient salts. Thus Odén explains the apparently xerophytic habit of many bog plants as really due in part to starvation owing to excessive retention of mineral salts by the humus (43). Kaserer (50) regards humus mainly as a reservoir for the nutrient material needed by the soil organisms. This is only one aspect of the subject, but it is of interest especially as regards the cycle of microbiochemical changes on which the supply of nitrogenous salts (nitrates and ammonium salts) to the plant depend. Undecomposed protein matter is probably present in the impure insoluble humin, while the amino-acids produced from it by the action of putrefactive bacteria are probably also absorbed by the humus colloid and supplied to the deaminating and nitrifying organisms.

Bases are very strongly absorbed by humus, especially ammonia, and then potash. This absorption, in view of recent work, may be largely chemical but it is not possible at present to say definitely to what extent this is so. One result of the preferential absorption of humus for ammonia and then potash is that the addition of ammonium or potash salts to the soil may result in the liberation of previously absorbed potash and/or calcium respectively which thus become more quickly available for plant nutrition (*cf.* 9, 1905). The irreversible coagulation which humus gel undergoes on drying has been shown to result in a considerable loss of its absorptive power for salts (*e.g.* 51, 52) so that in humic soils such drying out, whether caused by weather conditions or as a result of burning the surface of the soil, may result in the liberation of much absorbed plant food. Since the whole subject of absorption by soil is being critically discussed in a later paper, it is unnecessary to consider it in more detail here in relation to humus, the above remarks sufficing to indicate the general effects of its absorptive power on the soil solution. It should, however, be mentioned that Ehrenberg and Bahr (48) have advocated the hypothesis of solid solution, as opposed to absorption, as capable of explaining many of the phenomena hitherto ascribed to absorption.

The organic matter of the soil also affects the composition of the soil solution directly, by its erosive action on soil minerals with liberation of nutrient mineral salts, whether by humic acid itself, by absorbed plant acids or by carbonic acid produced by its oxidation.

CONCLUSION.

The present paper is intended to outline the general physico-chemical aspects of the relation of the organic matter of the soil to soil fertility. The subject is such an extensive one, and the factors governing soil fertility are so complex that the treatment in the restricted space available must necessarily be somewhat unequal. The literature cited is only a very small part of the whole, and many important papers dealing with the more specialised aspects of the question have had to be disregarded. For a more detailed account, together with a comprehensive bibliography, the reader is referred to Sven Odén's monograph (13) or to Ehrenberg's book (30).

The general effect of humus colloid on a mineral soil may perhaps best be summed up as that of a "buffer" substance, using the word in its widest sense. Its effects on the tilth, on soil moisture, soil temperature, and soil solution, are all such as to avoid harmful extremes, and to bring the properties of the most divergently composed mineral soils nearer to that happy mean which the agriculturist desires, and which tends to give the most stable and uniform cropping results under very variable climatic and weather conditions.

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THE APPLICATION OF PHYSICO-CHEMICAL METHODS TO THE STUDY OF HUMUS.

By Sven Odén.

What physico-chemical methods, and, one may almost say, chemical methods in general, have up to the present achieved in the explanation of the nature of humus, can by no means be compared with physical chemistry's magnificent achievements in other spheres, for example, in physiology. It is really only one special problem, namely, the question as to whether certain substances occurring on humus are of acid or non-acid nature, that physico-chemical methods have seriously attacked. It is therefore only with these that my paper will deal.

I think that the problem in question can most advantageously be treated historically, especially as during the last ten years a number of conflicting views have appeared.

The reason of the often heated nature of this conflict has probably been that the enunciation of the problem has been quite different with different investigators. To begin with, the outlines of the case will be here stated.

Vegetable substances undergo changes whose chemical nature is unknown. From relatively well-defined substances we get an inseparable complex: Humus.

From this complex different investigators have isolated many well-defined organic substances,[1] but, if the humus is treated with different solvents, there is always left a certain dark-coloured body, called by Schreiner and Shorey "unknown components". In the case of soil of low humus-content this does not comprise so great a proportion of the organic substance. In the case of soil rich in humus—especially peat or bog-earth—this residue comprises the great part of the soil. It has therefore been in connection with peat-cultivation that this question has aroused interest, and it was at a "Moorversuchsstation" that the problem in question originated.

Before going into this, another matter must be mentioned. It was clear, even very early on, that if humification takes place in a scarcity of bases, such as lime or magnesia, the humus has a sour character unfavourable for the cultivator, in contrast to the mild character, favourable to plant life, of the humus which has been formed in presence of lime.[2] It was easy to draw the conclusion that this difference was due to an acid character of the newly formed brown substances, which in the former case continued in the free state, and in the latter were neutralised by the lime. This view, which was first clearly formulated by Sprengel, was adopted by Berzelius.[1] We got the humic acids, especially when it was shown that the black bodies were dissolved on treatment with alkalies, but on addition of hydrochloric acid were again precipitated. Thus the name humic acids came to mean certain special substances.

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It had, however, early been shown, that the following well-defined acids occurred in sour humus[2]—phosphoric acid, acetic acid, malic acid, sulphuric acid—and several agricultural chemists had probably perceived that it was these bodies that gave to the sour humus its acidity, while the black substances were neutral or indifferent. Fresh weight was given to the problem in connection with the increasing importance of bog-culture at the end of the nineteenth and the beginning of the twentieth centuries, and the birth of the new science, *colloid-chemistry*. In 1909-10, the two Munich investigators, A. Baumann and E. Gully published two big papers,[3] which endeavour to lay down that (1) humus material was not of an acid nature, and (2) the acid reaction first appeared on addition of a salt which, by some sort of disintegration through adsorption, was broken down, because the undoubtedly colloidal humus-material adsorbed the base, and set free the acid. A hail of works for and against this view followed, and the confusion in the matter clearly had its cause in the fact that there were here two different problems, namely, (1) is humus-material to be regarded as acid or not? (2) where does humous soil get its undoubtedly acid reaction, for example, to litmus?

An affirmative answer to the first question does not necessarily mean that the acid reaction *is caused by* the humic acids, for their solubility may be so small that we do not get enough hydrogen ions for a decisive reaction with the indicator.

It is now the first point, namely the question of the acid nature of the humus, which has been solved with the aid of physical methods. The reasoning is as follows:—

Even if we have a very low concentration of hydrogen ions, these must react with hydroxyl ions in an added base with formation of water, and in time more and more hydrogen ions break away from the difficultly soluble body, while anions, in this case humic-ions, go into solution. If we choose ammonia as base, we get the following equilibrium:—

$$NH_3 + H_2O \rightleftarrows NH_4OH \rightleftarrows NH_4^{\cdot} + OH'$$

with a large preponderance on the left side. If for example, the concentration is 0.01 n., the ionised portion is only about 4 per cent.

Now, as regards the conductivity for electricity, conductivity is given by the $NH_4^{\cdot}$ and OH' ions. But since the ions are few in number, the conductivity, despite the great mobility of the OH' ions, is small compared with a solution of an ammonium salt of the same strength, where dissociation is fairly complete. If one now considers, on the one hand a water-suspension of some body, and on the other an equal volume of water, and to both equal volumes of ammonia are added, on comparing the systems the following three cases may occur:—

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1. The suspended body has no action on the base. In this case the conductivity of both systems is the same, provided that, when comparing the systems, we deduct the conductivity given to the system by the suspended particles.

2. The suspended body adsorbs the base, whereby the conductivity of the suspension becomes less than that of the ammonia solution.

3. The suspended body is an acid, which forms a salt with the ammonia. In this case an *increase* in conductivity must occur, compared with the ammonia solution.[1]

Experiments carried out with a suspension of prepared humic acid showed that case 3 was present, *and thereby was proved the formation of humic ions, and the acid nature of " humic acid "*.[2]

Some of the results are given in Table I.

TABLE I.

Added Ammonia, c.c.	Normal Strength.	Conductivity in Reciprocal Ohms.		Difference Δ.
		Water + NH_3.	Humic Suspension + NH_3.	
0	—	$2·0 \times 10^{-6}$	$9·0 \times 10^{-6}$	$7·0 \times 10^{-6}$
2	0·00357	65·8 ,,	216·4 ,,	150·6 ,,
4	0·00700	93·3 ,,	270·8 ,,	177·5 ,,
6	0·01030	113·3 ,,	299·9 ,,	186·6 ,,
8	0·01348	130·1 ,,	317·1 ,,	187·0 ,,
10	0·01654	144·9 ,,	332·1 ,,	187·2 ,,

The same occurs if we, instead of beginning with the prepared humic acid, take a suspension of the organic constituents of peat, after careful extraction with water, with a view to extracting soluble acids, only then the equilibrium is not attained at once.

The acid nature of humus material stands out still more clearly if we study the hydroxyl ion concentration of an alkaline solution much diluted in the one case with water, and in the other with a suspension of peat. In other words, if we titrate humus potentiometrically.

The result of a series of experiments of this nature is given in Table II. and Fig. 1. This is simply hydrogen ion concentration determined in the usual way with a hydrogenated platinum electrode, after which the hydroxyl ion concentration was calculated and plotted as ordinate in the figure. The continuous line shows the increase in hydroxyl ion concentration when we add increasing amounts of soda solution to a fixed volume of water.

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[1] As the fourth case may be taken that in which hydrolytic disintegration occurs through the influence of an alkali, whereby new substances are formed. This case which, as a matter of fact, with so small alkali concentration as here is the case, namely 0·02 n., and at ordinary temperatures would seldom be met with, would in any case take a long time, and not, as is the case with pure humic acid suspensions, at once attain equilibrium.

[2] Odén, Sven, *Arkiv. f. kemi etc. utg. av K. Svenska Vet. Akad. i Stockholm*, **4**, No. 26, 1912; **5**, No. 15, 1914; *Ber. d. deutsch. Chem. Ges.*, **35**, 651-60, 1912.

If we instead add the soda solution to a suspension of humic acids or peat, the hydroxyl ion concentration is at first hardly appreciably increased, as the OH′ ions are used up to form water with the dissociated hydrogen ions from the humic acids. Only when these are used up and the humate gone into solution does the hydroxyl ion concentration increase in the normal manner. From the amount of (hydroxyl ions) soda solution used for neutralisation one can clearly determine the amount of hydrogen ions used, in other words, titrate the humus. In the case in question 0·478 gm. of peat required 9·75 c.c. of 0·168 n. soda, representing 9·75 × 0·168 = 1·64 milliequivalents NaOH, or 3·4 mg. hydrogen per gm. of dry organic matter.

It is now to be observed that, if we take either a prepared humic acid or a well-washed humus earth (peat) and measure in the same way the hydrogen ion concentration potentiometrically, we do not get a higher value than $P_h = 4{\cdot}5$, corresponding with a hydrogen ion concentration of only 0·00003, while if we measure the hydrogen ion concentration in the peat direct we get noticeably higher values.[1] This shows that the acidity of sour earth is caused by other substances than those acids which are classically termed "humic-acid". We are therefore confronted with the second question, "what is the origin of the often-acid reaction of humus earth?"

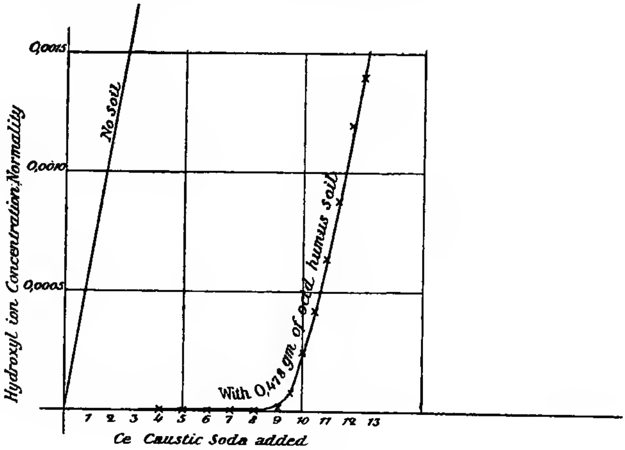

FIG. 1.

Baumann and Gully answered the question thus: "It is the humus which adsorbs the base in the salts and sets free the acid by colloid action, and similar circumstances occur in the cell membrane, and especially in the hyalincells of the Sphagna. This acidity becomes, therefore, most pronounced on manuring." Now, as I have shown elsewhere, all this theory of breaking up by adsorption is highly doubtful.[2] If one studies the cases given in the literature one finds that all those colloidal bodies which are said to adsorb bases and set free acids are either prepared from acid solutions, or treated with such during purification, while those colloids which are alleged to adsorb acids and set free bases have previously been treated with alkaline liquids.

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[1] Saidel, T., *Bull. de l'acad. roum* **2**, 38, 1913; Gillespie, L. J., *Journ. of the Washington Acad. of Science*, **6**, 7, 1916; Fischer, G., *Kühn-Archiv*, 4, 1-136, 1914; Odén, Sven, *Die Huminsäuren*, Dresden, 1919.

[2] Odén, Sven, *Journ. of Phys. Chem.*, **25**, 321 (1921).

TABLE II.

Potentiometric Titration for Determination of Total Acidity in Humus Soil.

A sample of soil containing 0·478 *gm. dry organic matter was treated with* 50 *c.c.* 0·2 *n. caustic soda, and warmed on the water bath for* 8 *hours. It was then neutralised with* 50 *c.c.* 0·2 *n. hydrochloric acid, after which hydrogen was passed in. The sample was treated with* (*v*) *c.c.* 0·168 *n. NaOH, whereafter Ph was determined in the usual manner.*

The total volume before the potentiometric titration was 300 *c.c.*

C.c. Soda Added (v).	Bridge Reading on Connecting		P_h.	Hydroxyl Ion Concentration in Terms of Normality.
	Normal Cell.	Gas Column.		
0	495·4	236·5	4·09	$1·1 \times 10^{-10}$
1	,,	241·5	4·27	$1·6 \times 10^{-10}$
2	,,	249·0	4·54	3×10^{-10}
3	,,	253·7	4·70	$4·3 \times 10^{-10}$
4	,,	260·1	4·93	$7·3 \times 10^{-10}$
5	,,	269·7	5·28	$1·6 \times 10^{-9}$
6	,,	282·3	5·73	$4·6 \times 10^{-9}$
7	,,	310·0	6·72	$4·5 \times 10^{-8}$
8	,,	314·6	7·85	$6·1 \times 10^{-7}$
9	,,	383·1	9·32	0·000018
9·5	,,	400·8	9·96	0·000079
10	,,	414·6	10·46	0·00025
10·5	,,	420·9	10·69	0·00042
11	,,	425·7	10·87	0·00064
11·5	,,	429·5	11·01	0·00088
12	,,	433·0	11·13	0·0012
12·5	,,	435·4	11·22	0·0014

It is, in other words, not here a question of a breaking-down of the added salt, but of the appearance of salts or bases already present, which are set free in exactly the same manner as when we wash a sample of blood charcoal with hydrochloric acid and then with water until no more chlorine ions are present in the filtrate, and then add neutral sodium sulphate, which forces out chlorine ions, which are again apparent in the filtrate.

What now are these acids which are forced out from humus on addition of salt and where do they come from? The question is not yet finally answered. They are probably partly of an inorganic nature, such as phosphoric acid (Einhof, Eggertz), [1] sulphuric acid, from the oxidation of pyrites (G. Fischer and H. Kappen) [2] and they are partly undoubtedly of an organic nature, such as acetic acid, propionic acid, oxalic acid, and others, formed by the life-processes of micro-organisms.[3] These acids are poisonous to plant life, while the dark, difficultly soluble humic acids are probably relatively innocuous.

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[1] Pontin, M., *Kongl. Sv. Landtbruks-Akad. i Stockholm Annaler*, 1, 240-55, 1813.

Fischer, G., *Kühn-Archiv.*, 4, 1-136, 1914; Kappen, H., *Landwirt Versuchsst.*, 96 277, 1920.

[3] Mulder, G. J., *Die Chemie der Ackerkrume*, 1 *und* 2, Berlin, 1861-62; Schreiner, O., and E. C. Shorey, *U.S.A. Dep. of Agricult. Bur. of Soils Bull.*, No. 53, 1909; compare also *Shorey in Hawai Agric. Exp. Stat. Rep.*, 1906, 37-59; Ritter, G. A., *Fühlings, landw. Ztg.*, 61, 593, 1912; *Int. Mitt. f. Bodenk.*, 2, 411-28, 1912; Densch, *Arbeiten d. Moorversuchsstation*, Bremen, 5, 331, 1913.

The usefulness of the liming of peaty soil depends, therefore, in my opinion, on the circumstance that we obtain a rich supply of lime humates. This mixture of humic acid and its lime salts makes an excellent regulator, which prevents both a strong acid reaction because of the breaking up of the lime humate with liberation of relatively innocuous humus acid, and an alkaline reaction because the small amount of hydrogen ions still present can react with hydroxyl ions, and so neutralise the base.

There is another theory with regard to the usefulness of liming bog soil. As is well known, the natural bog vegetation shows a xerophytic habit which, despite the supply of water, reminds one of desert types; thickened cuticles, small leaf area, etc., and it was believed that this was dependent on the circumstance that the water was so firmly held by the colloidal humus bodies that, despite the large amount of water present, the plants suffered from scarcity. Only on liming could the water be easily available for the plants, since the lime humates formed would not bind the water to the same degree as the free humic acids [1]

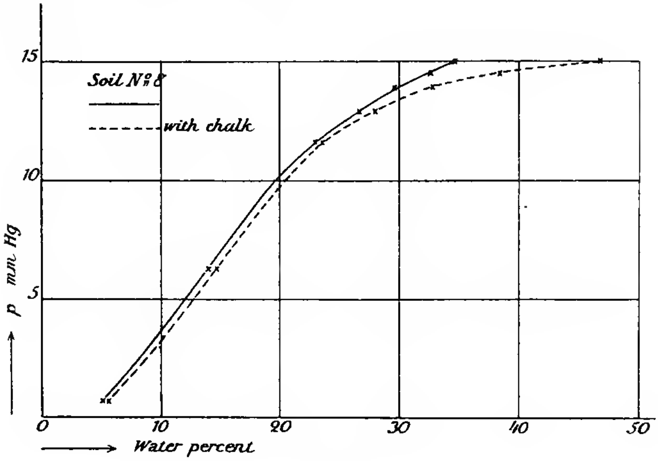

FIG. 2.

I have done some experimental trials with a view to seeing whether this theory was justified. The objective was to ascertain whether the binding of the water, as shown by the combined water's vapour tension, showed any marked difference when acid humus soil was neutralised with lime. Some vapour tension curves for limed and unlimed humus are given in Figs. 2 and 3. They were arrived at by allowing limed and unlimed samples to attain constant weight in an experimental atmosphere of varying water vapour tension (obtained with sulphuric acid-water mixtures) and then determining the amount of water. The lower the vapour tension the more firmly, clearly, is the water combined. As one sees, the curves for limed and unlimed samples show little difference, except that it is shown that after liming the water is somewhat more firmly bound than before.

It seems, therefore, to judge from these results that it is hardly probable that bog flora owes its xerophytic habit to want of water. It may just as easily be an adaptation to scarcity of food-salts. It may in this connection be pointed out that many of the typical bog plants, for example, *Calluna*

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[1] Süchting, *Fühlings landwirt Zeitung*, **61**, 465, 1912.

Vulgaris, *Ledum Palustre*, *Empetrum Nigrum*, *Myrtillus Uliginosa*, *Vaccinium Vitis Idæa*, are found on land poor in plant food, independent of the water conditions. On marshy land richer in food-salts we find, despite the acidity of the soil, a flora of more mesophytic character; one finds there, for example, *Viola Palustris*, *Cirsium Palustre*, *Agrostis Canina*, *Peucedanum Palustre*, *Caltha Palustris*, *Geum Rivale*, and others.

It is perhaps impossible to draw from the foregoing facts any certain conclusions. As possible causes for the xerophytic habit of bog plants other than scarcity of food-salts, may be advanced scarcity of oxygen for the root system, accumulation of detrimental acids such as oxalic and formic acids, etc. It is fairly certain that a large part of the (in any case) sparsely available food-salts are adsorbed by the humus material and become difficultly available. The formation of mycorhiza in many bog growths may also be attributed to an adaptation to scarcity of nitrates, and does not occur in a typical xerophile district, as for example deserts.

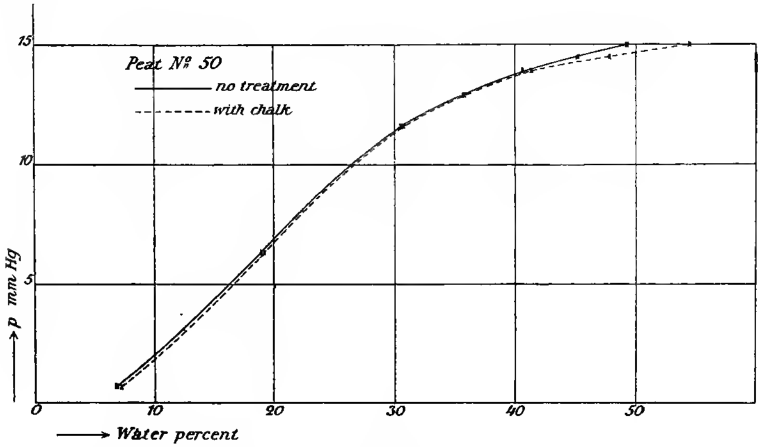

FIG. 3.

Liming acts then on these conditions in bog land in such a manner that the toxic acids are neutralised, and, simultaneously the humate of lime formed opposes formation of the same. As already mentioned, lime humates are specially well adapted to this purpose, since they are salts of acids which are soluble with difficulty and therefore difficult to wash out. Further, soluble calcium salts (for example $Ca(HCO_3)_2$) ought to have a tendency to force out adsorbed food-salts, whereby these become more readily available for the plants. On the other hand, no significant influence on the supply of water ought to be felt.

THE VERTICAL DISTRIBUTION OF SOIL ACIDITY IN NATURAL SOILS AND ITS RELATION TO THE ORGANIC CONSTITUENTS.[1]

By E. J. Salisbury, D.Sc., F.L.S.

Much has already been done towards the investigation of acidity as it varies between one area and another, but the modifications of this factor in the vertical direction have, up to the present, been almost entirely neglected.

It is unnecessary to emphasise here the importance of distinguishing between the factors which enable a true acidity to be realised and those which actually bring about the acidity itself. With regard to the latter, it is immaterial to the immediate question whether the acidity is due to the ionisation of organic or inorganic acids or to adsorption phenomena consequent upon the presence of colloidal humus.

It is, however, necessary to consider briefly the conditions which bring about the removal of bases and thus permit the development of high hydrogen ion concentrations.

The most important of such factors is the leaching action of carbonated rain-water which, as the Rothamsted results have shown, can remove calcium salts at the rate of 800 lb. per acre, per annum. This rapidity of leaching necessarily diminishes as the amount of calcium becomes the limiting factor and, as a consequence, the gradient of increasing calcium, as we pass downwards, is sometimes very similar in the first few inches whether the natural soil be derived from a highly basic deposit such as the Wenlock limestone or one comparatively poor in soluble salts.

The leaching results in a downward travel, and the curve of increasing bases becomes, as a whole, flatter the greater the capacity of the soil for percolation and the lower the basic content of the subsoil.

There are, however, two factors tending to establish a gradient in the reverse direction, both of which are biological.

The first of these is the influence of earthworms. I shall not enter into details of this here, as the data and experiments on this point will be published elsewhere, but it will suffice to state that the wormcasts deposited at the surface show an appreciably lower acidity, as measured by the hydrogenion concentration, than the same soil before its passage through the worm. This is apparently due to the action of the calciferous glands whose supply of calcium is presumably replenished from the subsoil.

The action of worms, then, tends to augment the basicity of the surface, and so with rain action to establish a gradient in the reverse direction to that consequent upon leaching.

The second biological factor, acting in the same sense, is the living mantle of plants. These are constantly exerting a pumping action upon the soil, and the bases brought up in this manner are roughly proportional to the size of the individual constituents of the vegetation though, of course, the amount will vary greatly with the specific character of the plant. With the onset of winter, that part of these bases which is contained in the leaves and twigs of the trees, or the entire overground shoot system in the case of herbs, is returned to the surface which is hence annually enriched by mineral salts. In poor soils overlying rich subsoils the surface may even in consequence show a higher basic content than the layers immediately beneath.

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[1] For a fuller discussion of the problems here considered *cf.* Salisbury, "The Stratification and Hydrogen-ion Concentration of the Soil in Relation to Leaching and Plant Succession (*Journal of Ecology*, vol. ix., pp. 214-234).

If we are to appreciate the real significance of the relation between the soil and its plant covering, we must distinguish between the herbaceous perennials and annuals on the one hand, which return into circulation the major part of the salts taken up, and the trees and shrubs on the other, in which a large portion becomes demobilised for a long period of years in the overground and underground organs. This is especially true of trees where the plant bodies represent a great storehouse of mineral salts demobilised, so far as the soil and other plants are concerned, until the death of the individual; a condition which is accentuated in the semi-natural woods of civilised countries where there is no continual succession of decaying trees. It might be argued that trees draw upon lower strata of the soil, but this difference is not so great as might be supposed since the actual feeding roots of our forest trees are mostly situated in the top three feet of soil. We may, perhaps, in part relate to this locking up of mineral salts the high acidity characterising many soils permanently covered with ligneous vegetation, a feature which is reflected in the poor fauna of heaths and woods.

From this point of view the decay of the plant remains is important, the contrast in this respect between the organic material derived from the overground parts of most herbaceous plants and that derived from the fallen leaves and twigs of such species as *Ulex europæus* and *Calluna vulgaris* scarcely needs emphasising.

Broadly, acidity and low basic content in natural soils are associated with slow and incomplete decay, whereas, under conditions favourable to rapid decomposition, the contained bases are released and mild humus results. Some years ago I was able to show that the acidity of woodland soils, as measured by their lime requirements, rose after coppicing, but subsequently decreased as the organic constituents diminished.

Under conditions of undisturbed natural vegetation, the covering of plant débris tends to accumulate and so, added to the continued leaching action, we have a continually increasing amount of non-available salts. Such areas tend to become more and more acid, and this increasing acidity is manifest in the tendency for old woodlands to pass gradually into a more and more heath-like condition, and is probably one of the most important factors militating against their natural regeneration.

If we examine a series of samples from a dune system with ranges of increasing age, we find that as we pass from the youngest to the oldest dunes the calcium content decreases owing to progressive leaching. On the other hand, with the increased stability of the older stages there is an augmented plant covering associated with which we find an increasing organic content. As the organic content increases, so too does the acidity. For example, newly formed dunes with practically no organic material will show a hydrogen ion potential of 7·4 to 7·6, whilst an old turf-covered dune with about 10 per cent. of organic material may show a P_H of from 6·6 to 6·8 or lower.

When we examine the acidity in the vertical direction, we find that this diminishes as we pass from the layers rich in humus to the lower layers poor in humus although the relation to the organic content is only a general one.

A number of estimations in the woodlands of Cornwall, many of which, apart from periodic coppicing at intervals of thirty to forty years, have remained more or less untouched, showed a range of acidity in the humus layer of the *Pteris* Society of from P_H 5·4 to 5·7, whilst at 12 inches the average hydrogen-ion concentration was P_H 6·1 and at 24 inches, 6·5. In the same area the *Vaccinium Myrtillus* Society gave from P_H 3·6 to 5·2 for the humus layer and from P_H 4·0 to 5·7 at 6 inches, whilst at greater depths the gradient was practically the same as under *Pteris*.

These estimations brought out clearly two points. Firstly, the decrease of acidity as we pass downwards, and secondly, the importance of the nature of the plant covering. Considering plants growing on the same soil the humus of *Vaccinium*, for example, appears to be more acid than that of *Pteris*. Similar estimations on lowland woods showed that the same relations obtained whilst the humus formed by *Deschampsia* and *Molinia* showed a much lower acidity.

A number of acidity determinations in a *Quercus robur* wood with a *Pteris-Scilla* ground flora gave an average of P_H 4·8 for the humus layer with a gradual increase to 5·8 at a depth of 9 inches. In the more basic Society of *Mercurialis perennis* and *Ficaria verna* even the surface layer was alkaline, but less so than the underlying soil. In samples from a *Pteris* Society on the Hythe Beds of Surrey the surface inch gave an average of P_H 5·7. In the underlying soil the acidity fell gradually, but even at a depth of 18 inches only attained P_H 6·0. By contrast the gradient on a Beech Wood is very steep, the maximum alkalinity being often attained at from 2 to 6 inches below the surface.

These few examples are typical of all the estimations, and out of several hundreds of these the only exceptions to the decreasing acidity from above downwards have been habitats where (1) the subsoil is highly basic and the humus particularly rich in salts and decaying rapidly, (2) flush vegetation, or (3) where there were corresponding irregularities in the humus gradient.[1]

In the first case the high proportion of bases and consequent low acidity is due to the pumping action of the plant, in the second to transport by water.

There are certain species such as *Ficaria verna* and *Adoxa moschatellina* which are shallow rooted species and which normally occur in situations of low acidity. These are sometimes encountered rooted in the surface layers of a flush or elsewhere even though the lower layers are appreciably acid, a condition which is the exception, however, not the rule.

A more striking case of the relation of rooting depth to the acidity gradient is furnished by *Arum maculatum* and *Mercurialis perennis*, both especially met with on soils of low acidity, but sometimes encountered in association with species like *Pteris* which are tolerant of moderately high acidities. It is therefore significant that in the cases investigated the *Pteris* roots were situated in the more acid soil near the surface, whilst the species less tolerant of acidity were rooted at a greater depth where the soil was more basic.

Such layering of the root systems of plants is a common and widespread phenomenon, and it is not improbable that rooting depths are, in part at all events, determined by the acidity gradient described or by the conditions correlated therewith. Broadly, the deeper rooting species such as *Orchis mascula*, *Allium ursinum*, *Colchicum autumnale*, etc., are more intolerant of acidity than the shallow rooting species such as *Holcus mollis*, *Oxalis acetosella*, etc.

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[1] Cf. Salisbury, *Jour. Ecology*, *loc. cit.*

The study of virgin natural soils has not the same economic stimulus that has promoted the mass of accumulated data with respect to the artificially modified soils of ordinary agricultural practice. Nevertheless, the prosecution of their detailed investigation may well throw light on problems which would otherwise remain obscure, and it is therefore to be hoped that more workers will attack the problems they present.

DISCUSSION ON "ORGANIC CONSTITUENTS OF THE SOIL".

The **Chairman**: The discussion on this question of the organic constituents of the soil is now open. I wonder if Dr. Salisbury, in the course of his investigations, has come into contact with a problem that has often impressed itself upon me, namely, that in many of the districts where we find peat in large accumulations we have evidence that the peat is of comparatively recent production, and that it certainly was preceded by forest growth. I think it can be noticed that many deposits of peat of the Welsh Hills, on Dartmoor, on the carrs of Nottinghamshire, and so forth, have a forest growth at the bottom, and that forest growth must have died out when the peat formation set in. Why did not the forest formation persist? We are still lacking in that fundamental knowledge on what turn of events starts the soil growing acid, after which peat formation begins. I have ventured the hypothesis that after the glacial ice retreated the soil was for a time comparatively neutral and maintained neutral forest growth and vegetation, but somehow or other as a result of the decaying vegetation acid conditions set in and with them the destruction of the forest growth, followed by the accumulation of peat. I wonder if Professor Odén has got anything to say of experience of that kind in Sweden.

Professor Sven Odén: I have no personal experience with regard to vegetation and acidity, but I think that Dr. Olof Arrhenius, in Sweden, has done some work of the kind we are now discussing. He has made extensive researches on the hydrogen-ion concentration of the soil of plant associations in the coast region of Stockholm,[1] in which he found definite P_H values characteristic of each type of plant association, and has thus been able to group various plant associations according to P_H. I am not able here to give details of the work, but I think he found a close relation in the same direction as was mentioned between the optimum for each plant and the P_H of the soil solution. He has also tried the colorimetric method for determining the P_H value.

With regard to the purely chemical nature of the humic acid, there are some recently published researches by a German scientific man, W. Eller,[2] which ought to be mentioned, as, for the first time, through a simple oxidation of a phenol :—

$$C_6H_4(OH)_2 + 2K_2S_2O_8 + 4KOH = C_6H_4O_3 + 4K_2SO_4 + 3H_2O$$

substances were obtained which, not only in composition (58·05 per cent. C. 3·25 per cent. H.), but also in their colloidal and other physical and chemical reactions, seem to be identical with the natural humic acids. We must wait a little and see whether the formula put forward can be maintained,

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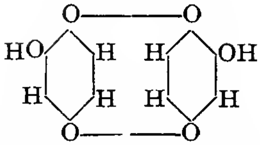
[1] Dissertation at Stockholms Högskola, 1920.

[2] W. Eller, *Ber. d. deutsch. Chem. Ges.*, 1920, 53, 1469; *Brennstoffchemie*, 1921, 1, No. 9.



but I think that the theories advanced by Eller are worthy of notice, and his experimental work on the constitution of the humic bodies is very promising.

Dr. J. A. Voelcker: I was somewhat surprised to hear the reader of the last paper mention that he had had experience of deep-rooting plants suffering from extreme acidity while shallow rooted plants did not. He certainly mentioned that there were exceptions to this, but I would call to mind that in our Woburn work on acid soils it was the deep-rooted wheat which grew for a considerable time under the influence of acid, whereas the shallow-rooted barley suffered the more quickly. Of course, there may be this difference, that in our case the acidity was not what one might call natural acidity, such as might be derived from organic matter, but was one which had been introduced by the application of sulphate of ammonia over a very long time, but, at all events, both wheat and barley had been subjected to the same amount of acidity, and the result was the reverse of that which the reader of the paper had experienced.

Dr. Wm. B. Brierley (*Rothamsted*): An aspect of this discussion to which one would like to see greater prominence given is the relation between many of the physico-chemical processes occurring in the soil and the soil fauna and flora. Mr. Keen has described the "soil-soil moisture" complex, but to visualise the conditions so is to oversimplify the matter: what we are dealing with is a "soil-soil moisture-soil organisms" complex, and many of the physical and chemical processes in the soil are causally dependent upon the last factor. Many organisms are present in certain soil types and not in others, and where present not only have a characteristic lateral and vertical distribution but also show a definite seasonal periodicity. For example, algæ are present in enormous quantity in soils. Certain algal species possess mucilaginous sheaths, others do not, and the varying abundance of these two types alone at different periods of the year must very considerably affect the soil-moisture system. Many fungi produce acid in quantity, and it would seem probable that the vertical distribution of acidity in the soil, described by Dr. Salisbury, must bear some relation to the vertical distribution of the fungi in the soil. There are also the bacteria and protozoa, each playing their distinct part in the soil economy. The whole problem of the physico-chemical reactions in the soil is undoubtedly made more difficult by the inclusion within one's purview of the soil organisms, but they cannot be neglected. Their presence has long been recognised, but we still know little about their activities. The investigations being carried out at Rothamsted will probably throw much light upon the obscure relations of these organisms to the total complex. I would emphasise the fact that even in a physico-chemical discussion such as this, the biological factors must not be omitted from consideration.

Dr. W. R. G. Atkins: In discussing this matter of sôil acidity, it is usually assumed that the acidity is of an organic nature, but I do not think that need necessarily be the case always. In one case I have come across lately there is evidence that the soil acidity is due to sulphuric acid from the oxidation of iron pyrites. Mr. W. A. Davis, working at Pusa, in India, has kindly sent me samples taken in Assam over a large area, and these work out uniformly at a P_H value of 5·4 or 5·6. In samples of these soils you find small particles of iron pyrites distributed, and some of the sub-soils were just coarse sand. An interesting point is that, whereas the indigo plants grew to an extraordinary height (12 to 15 feet) in the Assam soils, in Bihar they did not surpass 4 feet. Mr. Davis' view was that this effect was due to phosphate. Apparently this acidity in the Assam soils resulted in a higher amount of available phosphate. I believe that a large amount of work has been done, mainly in the United States, lately, as to the beneficial results of composting sulphur with rock phosphate. There are a great many other points of interest in the papers, but I will not deal with them, as the time is so short.

Dr. W. R. Ormandy: I was very pleased when your Secretary sent me an invitation to join in the discussion on these papers to-night, and I was particularly pleased to see the papers to be read by Professor Sven Odén. There have been several papers by Professor Odén, and with regard to all of them there is much to be said. In the first place, I should like to refer to the paper regarding the method for estimating the acidity of humus by means of conductivity tests. I do not wish to say that what I have to bring forward will prove in the end in any way to destroy the validity of this very important work, but it certainly has an important bearing upon it, and it has this distinct advantage, that it is work carried out upon a comparatively simple problem, for there are not more than half a dozen "unknowns," whereas it seems to me that in most of the problems we have been dealing with to-night there are hundreds of unknowns, and each speaker gets up and points out further ones. At the present moment we are very much unaware as to what happens when water vapour is adsorbed on to a complex phase, like the surface of a china clay particle. Much has been said to-night as to what happens with a mixture consisting of finely divided mineral matter, clay, humus, admixed with micro-organisms, algæ, and other things, but it is obviously difficult to arrive at a definite conclusion under such complex conditions. Therefore, for that reason, I have carried out my experiments on the simplest colloids which I could hit upon, namely, pure china clay, and on a very allied substance—ball clay. It is quite clear that the acidity test of Professor Odén depends on certain conductivity work, and in this connection I would like to direct your attention to the following: If 100 gm. of clay be shaken up with caustic soda solution of various strengths containing, say, ·1 per cent., ·2 per cent., etc., of the weight of the clay it will be found that the amount totally adsorbed will vary with the time of contact, thus a given clay will in twenty-four hours with shaking completely adsorb ·05 per cent. of its weight of caustic soda, whereas with ten days' contact a similar clay will adsorb ·15 per cent. If the alkalinity of the liquid in contact with the clay be allowed to rise, the ratio of adsorbed to free alkali is much greater after ten days than after one day. When ·3 per cent. of caustic soda is adsorbed by 100 gm. of clay only about $\frac{1}{3}$ of 1 per cent. of the amount of adsorbed alkali will be found free in the solution.

If now we take a one-day clay containing ·05 per cent. of alkali or a ten-day clay containing ·15 per cent. of alkali and subject these to treatment with boiling water in a soxlet no alkali will be washed out.

We have found considerable difficulty in estimating the small amounts of alkali which were free in the water when treating clays with an amount of alkali above the amount that they would totally adsorb, particularly when the amount of alkali added was considerable, and very fine dispersion was arrived at. We thought therefore that we might turn to an electrical method for determining the conductivity and consequently the amount of free alkali. Attempts were made to determine this conductivity with nickel anode and cathode in a watery suspension of clay containing ·2 per cent. adsorbed alkali. It was found that the conductivity of the solution, employing any voltage below 1·68, gave the usual type of curve independent of the time of passage of the current, but the moment the voltage exceeded 1·68 the conductivity increased with the time; in other words the adsorbed alkali, was set free. As the alkali thus set free is immediately re-adsorbed, there is a direct connection between the voltage in excess of 1·68 and the variation in conductivity with the time. We have had samples of natural clay sent from America which on refluxing in a soxhlet gave no traces of free alkali, but which on electrical treatment gave as much as 2·5 per cent. NaOH. The question arises as to whether this caustic soda can be taken as being chemically combined with the surface layers of clay. Professor Odén states at the end of his paper—"as I have shown elsewhere all this theory of breaking up by adsorption is highly doubtful". We have found that clay which has adsorbed the maximum amount of caustic soda to leave a neutral solution behind it will not adsorb copper, nickel, and other salts, but that such clay not treated with caustic soda does adsorb metallic salts. Similarly clay which is saturated with caustic soda will adsorb quite a lot of phenol phthalein without, however, becoming in any way coloured. If distilled water have clay suspended in it, and the mixture be titrated with caustic soda, alkali will be adsorbed, and it will appear as though it were an acid, but if the alkali be estimated electrically such adsorption will not be found if a voltage over 1·68 be employed. I would like to point out that this fact may have a bearing on measurements of cataphoretic velocities such as were carried out by Professor Hardy with globulin which had combined with alkali. It is fairly certain that colloidal particles will not move in an electric field in a liquid free from electrolytes, but it is quite possible that the necessary electrolytes may be set free by the current employed in producing the field in which the velocity is to be measured. If Professor Odén's figures are correct, it comes out that the humic acid adsorbed 1·1 per cent. caustic soda, and a normal sample of ball clay will have to contain 15 per cent. of humic matter in order to give exactly the same adsorption. As, however, a china clay gives practically the same alkali adsorption as ball clay, it is obvious that the adsorption in that case is not due to the humic materials which are present. The work of Mr. Craven and myself points to the fact that it is desirable to treat colloidal substances electrically for the removal of adsorbed bodies before investigations are carried out upon such bodies as to their adsorptive powers. In conclusion, I hope that you will consider that these points have some bearing on the very important matter raised by Professor Odén.

Professor Sven Odén: Dr. Ormandy has related some very interesting experiments, using china clay, in order, I think, to prove that my hypothesis regarding "disintegration through adsorption" is wrong. It is very difficult to answer him now, as I have only heard of these experiments on clays during the last five minutes. The only way to answer is to again take up the matter experimentally. If I had based my conclusions solely on the conductivity measurements, which have been criticised by Dr. Ormandy, my case would be a weak one. Going into details, I should first like to point out that Dr. Ormandy uses a very large amount of material, namely, 100 gms. of clay, in a small volume of solution. With humic acids I have concentrations of the order of 0·002. Moreover, I am not quite clear about the origin of the clay which Dr. Ormandy has referred to. Has it been subjected to acid during weathering or not? But I will not go into details in this matter now, as it is very difficult to understand the whole matter without knowing the full experimental details. The main point of my paper on humic bodies is, that, in dealing with them I get a curve like *this* (Fig. 1).[1] As abscissa is the added soda. If I now add NaOH to a very small portion of humic bodies, and measure the hydroxyl concentration, it rises like *this* at a definite concentration. It is not quite sharp, because we have a little hydrolysis here. The main point is, that, even at this point, we have a great number of physical and chemical properties that are simultaneously changing, such as viscosity and colour, etc., and *this* point is nearly the same as I have determined by the conductivity method. The adsorption theory does not indicate any critical change at any concentration. I do not think a clay would behave in the same manner, but even for them I think that the theory of breaking up by adsorption is highly doubtful. It may be that Dr. Ormandy may be able to prove its correctness for clays, but what we here have to deal with is the humic portion of the soil, and I do not think we can get away from the fact that here we have an acid to deal with. Personally, I do not think that the theory of disintegration through adsorption is correct at all. At all events it is not *proved* to be correct in any case yet published.

Dr. W. R. Ormandy: I do not wish to say for one moment that the experiments I have done on clay will in any way prove what Professor Odén has done to be wrong. I merely point out that there is a very great similarity, but there is no time to go into all these points. One can show that the physical properties of the clay run exactly parallel with the statement which Professor Odén has made as to what he has found occurs in the case of humus material, but I do suggest that even from the point of view of the soil chemist it is worth while doing a great deal of this work on comparatively cheap bodies, and comparatively simple bodies, prior to undertaking a study of the properties of soils themselves. It would be better to experiment first on materials obtained in a state of very great purity, and china clay, which is got from a depth of 150 ft. below a decomposed granite formation, is not likely to have been subjected very much to acid treatment. The ball clay from near the surface may have been, but the ball clay with which I worked was taken from about 30 ft. down under a solid bed of impenetrable clay.

Dr. E. J. Salisbury, replying to the discussion, said: With reference to what you said yourself, Mr. Chairman, I should like to read a paragraph from my original manuscript:—

"Under conditions of undisturbed natural vegetation, the covering of plant débris tends to accumulate, and so added to the continued leaching action, we have a continually decreasing amount of non-available salts. Such areas tend to become more and more acid, and this increasing acidity is manifest in the tendency for old woodlands to pass gradually into a more heath-like condition, and is probably one of the most important factors militating against their natural regeneration."

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[1] See p. 291.

I think undoubtedly the work of Hessellman has shown that this has happened in Scandinavia, and there is little doubt it has occurred also in our own country. With regard to Mr. Brierley's comment, I should like to say that such estimations as I have made seem to indicate that except at the surface the humus gradient in the soil in the vertical direction corresponds very closely with the gradient in the amount of the live roots which one obtains from natural plant associations. This seems to indicate that, at all events, the humus derived from the decayed plant roots is the main factor in determining the vertical distribution of organic content.

SECTION IV.—PAPERS AND DISCUSSION ON "ADSORPTION PHENOMENA".

THE PHENOMENA OF ABSORPTION IN SOILS: A CRITICAL DISCUSSION OF THE HYPOTHESES PUT FORWARD.

By E. A. Fisher, M.A., B.Sc. (Oxon.), The University, Leeds.

The phenomenon of absorption in soils has been known from very early times and has long engaged the attention of investigators, partly on account of its own intrinsic interest and practical importance, and partly because it presents aspects that have in the past been difficult to reconcile with stoichiometric and other chemical laws. An enormous amount of work has been done on this subject, and most of the facts were collected by 1880; since then the work has centred mainly round the cause of the phenomenon. The work done up to 1906 was brought together and reviewed in considerable detail by Patten and Waggaman[1] in America, and a more recent résumé was published by Prescott[2] in this country in 1916.

The first quantitative experiments appear to have been carried out by H. S. Thompson[3] in 1845, who showed that ammonium sulphate solution filtered through soil exchanged its ammonia for lime.

J. T. Way[4] made a detailed study of the subject by allowing solutions of ammonia and of nitrates, chlorides and sulphates of ammonia, potassium, sodium and magnesium to percolate through layers of soil, and found that the bases were very largely removed by the soil and replaced by lime. In the case of ammonium chloride the chloride content was unaffected. Way demonstrated that the active part of the soil was the clay, and attributed the activity to a particular constituent which he thought was a hydrated aluminosilicate of alkali or alkaline earth. He prepared a series of artificial aluminosilicates which behaved similarly, and attributed the phenomenon entirely to interchange of bases by ordinary double decomposition. Way emphasised this since even at this early date attempts were being made to explain the facts by surface absorption (Matteucci[5]); as Way pointed out the physical explanation of the time could only explain the absorption of a salt as a whole, and would not explain the non-absorption of the acid radical nor the exchange of bases which always accompanies the absorption.

This experimental work of Way has been repeated and extended by many workers since, and among the earlier ones may be mentioned Henneberg and Stohmann[6] on ammonium salts, Eichhorn[7] with natural minerals such as natrolite, A. Voelcker[8] who attributed the beneficial effects of common salt as a manure to its action in setting free potash from its combinations in the soil,* and Warington[1]. All these workers accepted the chemical explanation of Way, although Warington also regarded the oxides of aluminium and iron as being involved on account of the absorbing powers of these oxides, as well as soil, for phosphates.

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[1] Patten and Waggaman, *U.S. Dept. Agric. Bur. Soils Bull.*, **52** (1908).

[2] Prescott, *J. Agric. Sci.*, **8** (1916), p. 111.

[3] Thompson, *ibid.*, **11** (1850), p. 68.

[4] Way, *ibid.*, p. 313; **13** (1852), p. 123; **15** (1854), p. 491.

[5] Matteucci, *Sur les phénomènes physique des corps vivants*, 1847.

[6] Henneberg and Stohmann, *Ann. Chem.*, **107** (1858), p. 152; *and J. für Landw.*, 3 (1859), p. 25.

[7] Eichhorn, *Pogg. Ann.*, **105** (1858), p. 126.

[8] Voelcker, *J. Roy. Agric. Soc.*, **21** (1860), p. 105; **25** (1864), p. 333.

These essentially rational views of Way were, however, combated by Liebig[2] who considered that the retention of bases by the soil was similar to that by charcoal, that it was of a physical character due to surface attraction, and that in fact only those materials so held can be regarded as available plant food. Liebig's views received very general acceptance owing to his dominating position in chemistry at this time, although some workers, notably Knop[3] attempted a compromise between the two aspects. Knop adopted the physical view of Liebig for the absorption of bases followed by combination with silica or aluminium silicate, but attributed the retention of phosphates to chemical precipitation first with lime and then with iron or alumina. The main objection of the early physical school to the chemical interpretation was that with bases an equilibrium is always established between the soil and solution, more salt was absorbed from concentrated than from dilute solutions, and no matter how dilute the whole of the base was not completely removed. This did not accord with the stoichiometric views of the time, but is not an insuperable difficulty at the present day. Two conclusions were arrived at by Way which have since been found to be erroneous, but which probably militated against the general acceptance of his explanation. One was that the change was not reversible, the other that felspars, though similar in composition and properties to his artificial alumino-silicates, do not absorb ammonia. Numerous workers[4] since the time of Way have, however, demonstrated the reversible nature of the process. The latter objection was no less serious as it implied that the action is due to zeolites, and these have never been proved to exist in soils.[5] The classical work of Lemberg,[6] begun in 1870, proved conclusively that many other silicate minerals have the same properties of base exchange in salt solutions as the zeolites. This work of Lemberg is probably the most important that has been done on this subject, and it is unfortunate that it is not more accessible and familiar to agricultural workers. Lemberg's experiments were carried out at various temperatures, and the times of extraction varied from a few hours to two years and more. His results may be summed up under five heads:—

1. Exchange of bases in equivalent quantity between silicate and salt solution.
2. Addition of free base to the silicate from alkaline solution.
3. Addition of entire salt.
4. Addition or subtraction of water, and
5. Frequently a transformation into a different mineral species recognisable by its crystalline form ensued.

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* Lawes and Gilbert (*J.C.S.*, 45 (1884), p. 305) demonstrated the increased potash content of plants due to manuring with sodium and magnesium sulphates.

[1] Warington, *J.C.S.*, **21** (1868), p. 1.

[2] Liebig, *Ann. Chem. Pharm.*, **105** (1858), p. 109; **106** (1858), p. 185; also "Natural Laws of Husbandry," 1863.

[3] Knop, *Lehrbuch der Agrikulturchemie*, Leipsic, 1868.

[4] See more particularly Frank, *Landw. Versuchs. Stat.*, **8** (1866), p. 45; Küllenberg, *Jahrb. Fortschr. Agrik. Chem.*, **8** (1865), p. 15; Parker, *J. Agric. Res.*, **1** (1913), p. 179.

[5] Merrill, "Rocks, Rock-Weathering and Soils," New York, 1906, pp. 362-65.

[6] Lemberg, *Zeit. deutsch. geol. Gesell.*, **22** (1870), pp. 335, 803; **24** (1872), p. 187; **28** (1876), p. 537; **29** (1877), p. 483.

The most striking experiments were with leucite which was converted into analcite by NaCl-solution, and with analcite which with KCl-solution passed into leucite. These experiments were the more striking because leucite contains little water while analcite contains 8-9 per cent., and all the experiments at all temperatures with these minerals showed an increase in water content as sodium replaces potassium. These results are given in Tables I. and II.

TABLE I.

ACTION OF SALT SOLUTIONS ON LEUCITE (LEMBERG).

	Leucite.	NaCl.	NaCl.	NaCl.	Na_2CO_3.	NaCl.	NaCl.
Temperature °C. Time (months)		180-195 18 hours.	100 4	100 1½	100 4	40 11	Room 11
H_2O	0·32	7·86	7·84	8·04	7·54	3·40	1·79
SiO_2	56·04	55·30	54·62	55·38	54·72	55·83	55·68
Al_2O_3	23·38	22·91	23·46	22·71	23·61	23·50	23·48
CaO	0·20	0·29	0·20	0·25	0·20	0·10	0·15
K_2O	18·90	0·68	0·66	0·89	1·40	11·61	15·88
Na_2O	1·41	12·96	13·22	12·73	12·54	5·56	3·02
	100·25	100·00	100·00	100·00	100·01	100·00	100·00

TABLE II.

ACTION OF SALT SOLUTIONS ON ANALCITE (LEMBERG).

	Analcite.	K_2CO_3.	K_2CO_3.	KCl.	K_2CO_3.	K_2CO_3.
Temperature °C. Time (months).		100 7	100 4½	100 3	40 7	Room 13½
H_2O	8·80	0·98	0·89	0·98	1·23	1·69
SiO_2	56·32	56·03	55·87	56·38	56·59	56·43
Al_2O_3	22·00	22·20	22·29	22·39	21·97	22·62
CaO	0·51	0·60	0·60	0·45	0·52	0·40
K_2O	—	19·60	20·31	19·80	20·23	17·82
Na_2O	13·19	0·57	—	—	—	1·04
	100·82	99·98	99·96	100·00	100·54	100·00

One of the most striking things about Lemberg's experiments is that they show without exception that Na-silicate minerals are less stable in salt solutions than the corresponding K-minerals; in other words, under similar conditions potassium will replace sodium more easily and completely than *vice versa*. This is suggestive on account of the well-known facts that potassium is strongly absorbed by soils while sodium is not, and that the ocean is a solution of NaCl rather than KCl.

Van Bemmelen[1] in 1877 published the first of a series of papers on absorption of salts by soils, and further developed the point of view of Way and Lemberg. A soil boiled with HCl gives up silica to NaOH-solutions after washing off the acid, and its absorptive power for bases from alkaline solution is increased while that for neutral salts, such as KCl, has almost entirely disappeared. This latter absorptive power returned after treatment with NaOH, in which case potassium is absorbed and sodium goes into solution. The outstanding facts of van Bemmelen's work are that in no case is there absorption of neutral salt as a whole, but always an interchange of bases with the bases already present, and that the seat of the action is the *colloidal* silicates present. This is interesting, in view of the later work of Cushman,[1] who showed microscopically and from the formation of soluble alkali silicate that a certain amount of peptisation occurs when water and orthoclase or some other minerals are ground together.

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[1] Van Bemmelen, *Landw. Versuchs. Stat.*, **23** (1878), p. 265; **35** (1888), p. 67 *Zeit. f. Anorg. Chem.*, **23** (1900), p. 321; also *Die Absorption* (Steinkopf, Dresden), 1910.

The chief objection to Way's chemical theory was the fact that no stoichiometric relations appeared to exist between the amounts of different bases absorbed. This difficulty was due to the fact that solubility relationships were not taken into account. This factor was first emphasised by Armsby[2] in 1877. He worked with $CaCl_2$ and an artificial Na-alumino-silicate, and pointed out that there is opportunity here for the formation of two slightly soluble substances, *viz.* the Na- and the corresponding Ca-alumino-silicate. In such a case reaction does not proceed to the formation of one of these two substances exclusively, but an equilibrium mixture of the two is formed, and at equilibrium a definite relationship prevails between the concentrations of the reacting substances in the solution. Thus the Ca of the $CaCl_2$ will replace Na to some extent, but if NaCl is present in the solution from the start less replacement occurs. The lack of stoichiometric relationships between the bases absorbed is therefore explanable by the varying solubilities of their respective alumino-silicates, *e.g.* leucite + NaCl and analcite + KCl in the proper proportions should form the same equilibrium mixture. As a matter of fact this does not always occur in practice since, owing to the small solubility of the silicates, the reaction is slow and we rarely get real equilibrium mixtures. Thus the composition of the solid phase changed steadily with time, as already indicated in Tables I. and II. The reaction can be hastened by further grinding of the silicate and by increasing the concentration of the solution. In the latter case the higher diffusion gradient due to the increased osmotic pressure results in greater penetrating power. Such factors will influence the extent of the reaction in a given time.

Following on the classical work of Lemberg the base exchange theory in connection with silicates was further developed by E. C. Sullivan[3] in a paper which is now out of print. He worked mainly with orthoclase and a large number of salts but studied other minerals as well, including glass, a shale, and a clay gouge. In practically all cases he found a base exchange which, however, was not strictly quantitative. Some of these results are given in Table III., and all may be classified under four heads:—

1. Quantitative base exchange occurred between neutral salts, *e.g.* KCl, and neutral silicate.
2. Slightly more base was dissolved than precipitated when the solution of silicate was slightly alkaline, as with orthoclase.
3. Considerably more base was dissolved than precipitated when the salt was hydrolysed to an acid solution, as with gold chloride.

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[1] Cushman, *U.S. Dept. Agric. Bur. of Chem. Bull.*, 92 (1905).
[2] Armsby, *Landw. Versuchs. Stat.*, 21 (1877), p. 397.
[3] Sullivan, *U.S. Geol. Survey, Bull.*, 312 (1907).

4. Less base was dissolved than precipitated when basic salts were formed as was frequently the case with $CuSO_4$. Sullivan rightly points out that these changes involve the action of the alkali or alkaline-earth salt of a weak acid (silicic or alumino-silicic), and are therefore comparable with the more familiar behaviour of sodium carbonate with solutions of metallic salts. Thus we get

$$CaCl_2 + Na_2CO_3 = CaCO_3 + 2NaCl$$
$$2NiCl_2 + 2Na_2CO_3 + H_2O = NiCO_3, Ni(OH)_2 + CO_2 + 4NaCl$$
$$2FeCl_3 + 3Na_2CO_3 + 3H_2O = 2Fe(OH)_3 + 3CO_2 + 6NaCl$$

and the action of a silicate may be expected to be similar, except that owing to the greater weakness of the silicic acid the precipitate will tend to be more and more basic, that is, will tend to contain more hydroxide, and silicic acid or silica in a colloidal condition may be formed as well instead of CO_2. This may be the origin of the colloidal silica or silicic acid supposed to exist in the soil and which, it has been suggested, may exert protective action on the clay producing some of those flocculation anomalies[1] in soils that have so far not been satisfactorily explained. At the same time true silicate of the metal is formed as well, and both this and, in some cases, the basic salt formation was demonstrated by Sullivan.

TABLE III.

SUMMARY OF RESULTS WITH ORTHOCLASE AND SALT SOLUTIONS (SULLIVAN).

Solution.	Original Content, Mgm. Atoms.	Metal Precipitated, Mgm. Atoms.	Bases Dissolved, Millimoles.
Magnesium sulphate	1·98	0·40	0·47
Calcium chloride	2·44	0·51	0·54
Manganous sulphate	2·54	0·62	0·53
Ferric sulphate	1·21	1·16	1·41
Nickelous sulphate	2·06	0·93	0·92
Cupric nitrate	1·99	0·98	1·01
Cupric sulphate	1·98	1·03	0·85
Zinc sulphate	3·05	0·93	0·99
Strontium chloride	2·32	0·48	0·51
Silver sulphate	0·98	0·94	1·01
Barium chloride	2·04	0·71	0·78
Auric chloride	1·36	0·27	1·21
Lead nitrate	2·00	1·43	1·14

It is of interest at this point to inquire into the effect of concentration on the final equilibrium. It is evident that the type of reaction dealt with is essentially that between reciprocal salt pairs. W. Ostwald,[2] as long ago as 1884, showed that the solubility of the alkaline earth sulphates in mineral acids was essentially an exponential function of the concentration of acid, and a similar relationship was found by Meyerhoffer[3] to hold for the action of K_2CO_3 on $BaSO_4$. The silicate reactions should be similar, but the concentration curves both with pure silicates and soils do not as a rule appear to be strictly exponential. Various formulæ have been put forward to explain these reactions, notably by Bödeker[4] in 1859 and for ammonium salts by Hall and Gimingham[1] in 1907, but these hold only for a comparatively restricted range of concentration.[2] The equation introduced by Freundlich[3] to express the relation between adsorption and concentration appears to apply with a fair degree of accuracy to a large number of soil absorptions. This equation is $\frac{y}{m} = k\,C^{\frac{1}{p}}$, in which y is the amount of base absorbed by m gms. of soil, C is the final equilibrium concentration of the solution, and k and p are constants, and Prescott[4] points out that Hall and Gimingham's equation is a special case of this equation in which $p = 2$. By generalising from this, by making the constants vary between wide limits, this adsorption equation—and its corresponding curve—can be made to fit approximately very many soil and silicate absorptions. This equation, though, is not really exponential, while that for reciprocal salt pairs should be. From this it is argued that absorption of bases by soils or silicates must be of the nature of *ad*sorption.

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[1] Comber, *J. Agric. Sci.*, **10** (1920), p. 425.

[2] Ostwald, W., *J. prakt. Chem.*, **137** (1884), p. 55.

[3] Meyerhoffer, *Monatsch*, **17** (1896), p. 13; Meyerhoffer and Saunders, *Zeit. f. phys. Chem.*, **28** (1899), p. 453 and **31** (1899), p. 370; Meyerhoffer, *ibid.*, **38** (1901), p. 307 and **53** (1905), p. 530.

[4] Bödeker, *J. für Landw.*, **3** (1859), p. 48.

That the Freundlich equation is a purely empirical one is not sufficiently emphasised by agricultural workers; as the exponent $\frac{1}{p}$ is altered, a series of curves like a series of French curves is obtained, to one of which nearly any set of experimental points can be fitted with the desired degree of accuracy.[5] But apart from this and the experimental difficulties inherent in soil work, there are various reasons why the strictly exponential form of curve should not be obtained. Side reactions, such as the formation of basic salts or hydrolysis of salts of weak bases or acids, are bound to distort the curves. Alteration in effective surface of the soil during time of extraction has undoubtedly been a potent factor of disturbance in many cases, although its importance has not been properly appreciated.[6] Further, some soil and many other absorptions cannot be expressed by the Freundlich equation, and the equation also applies to many reactions that are not adsorptions. Thus the interaction between orthoclase and $CuSO_4$ studied by Sullivan can be expressed by the equation

$$\frac{y}{m} = 0{\cdot}0316\ C^{0{\cdot}2135}$$

and a similar expression fits the neutralisation of HNO_3 by soil. Peters'[7] results for the absorption of potash by a soil cannot be expressed at all by the Freundlich equation. They are given in Fig. 1. In Fig. 2 is given the curve obtained by taking the logarithms of both sides of the equation, *i.e.*

$$\log\left(\frac{y}{m}\right) = \frac{1}{p}\log C + \log k.$$

This curve should be linear if the Freundlich equation holds. In this case obviously it does not. But this particular log curve is made up of two approximately straight lines corresponding to the approximately vertical and horizontal portions of the absorption curve. It is perhaps not without significance that many soil absorption curves have been plotted through experimental points, all of which lie on one half of the curve only, *i.e.* on one or other side of the sharp bend, and many of Russell and Prescott's[1] phosphate curves are of this type. It is obviously not legitimate to draw deductions from the straightness of the log curve unless experimental points have been obtained in all regions of the absorption curve.

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[1] Hall and Gimingham, *J. Chem. Soc.*, 91 (1907), p. 677.

[2] Cameron and Patten, *J. Phys. Chem.*, 11 (1907), p. 581.

[3] Freundlich, *Kapillarchemie*, 1909.

[4] Prescott, *loc. cit.*

[5] Moore and Bigland, *Biochem. J.*, 5 (1911), p. 32.

[6] Fisher, *J. Agric. Sci.*, 11 (1921), pp. 19, 45; McCall, Hildebrandt and Johnston, *J. Phys. Chem.*, 20 (1916), p. 51; Cameron and Patten, *ibid.*, 11 (1907), p. 581.

[7] Peters, *Landw. Versuchs. Stat.*, 2 (1860), p. 127.

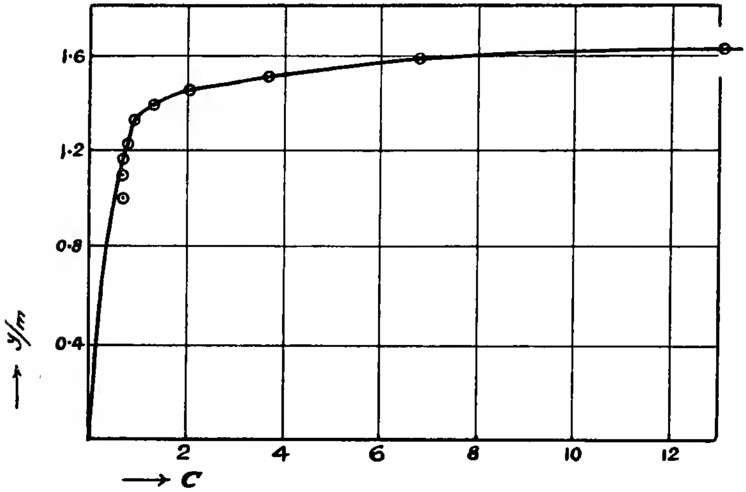

FIG. 1.

The base exchange theory does not of course explain the absorption of acid radicals such as phosphate, citrate, and oxalate, and Rostworowski and Wiegner[2] showed that such radicals are not absorbed by silicates, but a similar explanation is possible, based on the formation of insoluble salts with soil bases as first suggested by Warington.[3] Van Bemmelen[4] treated

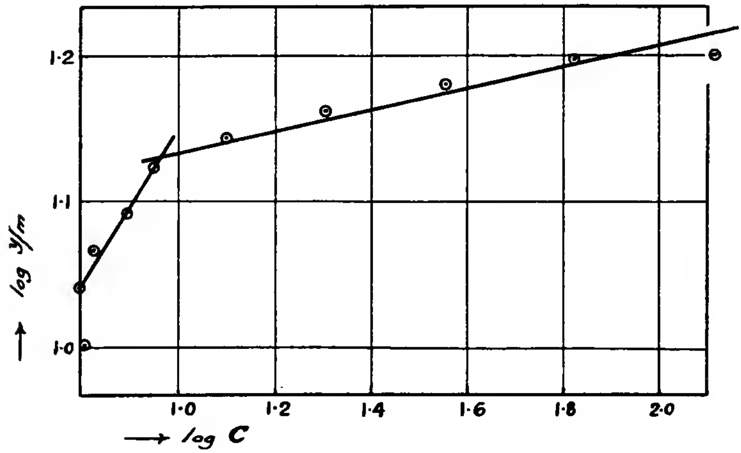

FIG. 2.

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[1] Russell and Prescott, *J. Agric. Sci.*, 8 (1916), p. 65.
[2] Rostworowski and Wiegner, *J. für Landw.*, 60 (1912), p. 223.
[3] Warington, *loc. cit.*
[4] Van Bemmelen, *loc. cit.*

soils with acids until the bases were dissolved so that base exchange could not occur, and found that such a treated soil would not absorb phosphates, carbonates, and borates. Later Hall and Amos[1] explained the retention of phosphates by the soil and their distribution between the soil and water by assuming the presence of P_2O_5 compounds of varying degrees of solubility. Such a view explains their experimental results satisfactorily, and is quite in accord with the views and results of Lemberg,[2] Armsby,[3] and Sullivan[4] and with the point of view developed in the present paper. Russell and Prescott,[5] however, controvert this view, and seek to explain the absorption of acid radicals as an *ad*sorption. A detailed criticism of this work supported by experimental evidence will be made elsewhere at a later date; here it is sufficient to point out that Russell and Prescott's results in no way conflict with the older point of view. They lay stress on the fact that citric acid extracts considerably more P_2O_5 from the soil than equivalent concentrations of nitric acid, "a fact which indicates that something more is concerned than a mere mixture of phosphates". But such a result is just what one would expect if a mixture of phosphates were present. All inorganic nitrates are soluble in water while many of the phosphates and citrates of lime, iron, aluminium, etc., are practically insoluble. An equilibrium is therefore brought about between the citrates and phosphates, some PO_4''' being replaced by $C_6H_5O_7'''$. A similar result would be expected by treating with nitric acid to which some soluble citrate has been added instead of using citric acid. Further, the presence of $CaCO_3$ diminishes the amount of P_2O_5 dissolved by citric acid as was noticed years ago by Cousins and Hammond.[6]

Similar considerations apply to oxalic acid. Prescott[7] found that considerable oxalic acid was absorbed by a deep Rothamsted sub-soil in the presence of $\frac{N}{20}$ HNO_3 which was added "to prevent the chemical precipitation of insoluble oxalates". As a matter of fact, when $Ca(NO_3)_2$ is added to a solution of oxalic acid in $\frac{N}{20}$ HNO_3, a copious precipitate of Ca-oxalate comes down in the course of an hour or so and the precipitation continues for some hours. To bring out still more clearly the essentially chemical nature of the process, Prescott's experiments with oxalic acid have been repeated with a Yorkshire soil devoid of $CaCO_3$: no appreciable absorption at all could be detected, although considerable precipitation occurred when $CaCO_3$ was previously added to the soil.[8] It is significant of the danger of drawing such definite conclusions from an adsorption curve that Russell and Prescott found that the nitric acid was itself partially neutralised, and their data show that the neutralisation depends upon the concentration and can be expressed quite satisfactorily by the adsorption equation

$$\frac{y}{m} = 2{\cdot}02\ C^{0{\cdot}22}.$$

No one would suggest that nitric acid is adsorbed by a soil, and yet the only difference between the two cases probably is that the P_2O_5 is precipitated as insoluble phosphate, while the nitric acid is merely neutralised, remaining in solution as soluble nitrate.

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[1] Hall and Amos, *J. Chem. Soc.*, 89 (1906), p. 205.

[2] Lemberg, *loc. cit.* [3] Armsby, *loc. cit.* [4] Sullivan, *loc. cit.*

[5] Russell and Prescott, *loc. cit.*

[6] Cousins and Hammond, *Analyst*, 28 (1903), p. 238.

[7] Prescott, *loc. cit.*

[8] N. M. Comber, private communication to the writer.

The absorption of acid radicals thus appears to fall into line with the absorption of bases.

The absorption of ammonia by soil is in some respects anomalous and is worthy of separate treatment. König[1] in 1882 noticed that humus will absorb ammonia from ammonium sulphate, and the absorbing power of organic material for soluble organic matter and ammonia is notorious, and base exchange does not always appear to take place. As against this Hissink[2] showed that ammonia is absorbed by an artificial silicate (permutite) in the usual manner by means of base exchange, and that the reaction could be expressed satisfactorily by an equation of the Freundlich type. A similar base exchange was found to occur by Hall and Gimingham[3] with $CaCO_3$ and NH_4Cl,* the equation in this case being

$$\frac{y}{m} = 1{\cdot}68\ C^{0{\cdot}526}.$$

The absorption by soil, however, is more complex, and no quantitative relationship has so far been found. Russell[4] found that the ammonia absorbed by soil from ammonium sulphate cannot be completely liberated by distillation with magnesia, and this is not easy to explain on the basis of base exchange only. At the same time ammonia does lower the surface tension (electrolytes generally raise it) as much as 8 or 9 per cent., and it is therefore not unlikely that both types of absorption occur—base exchange with the colloidal silicates and possibly humates and true adsorption with the organic matter and possibly other colloids as well.

The early physical views of Liebig[5] received much support by the introduction of the idea of colloids by Graham[6] (1861-64), and the extension of this idea to soils by van Bemmelen[7] (1877 onwards). The work of Van Bemmelen is often cited in support of the adsorption theory, but this is hardly justifiable, as in his day the idea had not the precise physical significance it has gained since. Van Bemmelen appears to have merged the idea of physical adsorption into the wider one of absorption, a term which he generally used to denote all kinds of loose chemical and physical combination resulting in the formation of colloidal complexes. His ideas have been largely exploited by subsequent workers, and undue precision given to them that they may appear to support more modern adsorptionist views.

A great impetus was given to the physical view when the general theory of surface adsorption had been put forward and developed by Willard Gibbs,[8] J. J. Thomson,[9] Freundlich,[10] Wo. Ostwald,[11] and others. The theory was immediately seized by agricultural chemists and applied by them to explain soil absorption. It was applied to soil acidity by Baumann and Gully[12] in

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* The importance of $CaCO_3$ in many geochemical transformations was demonstrated and emphasised by both van Bemmelen and Lemberg.

[1] König, *Landw. Jahrb.* 11 (1882), p. 1.

[2] Hissink, *Landw. Versuchs. Stat.*, **81** (1913), p. 377.

[3] Hall and Gimingham, *loc. cit.*

[4] Russell, *J. Agric. Sci.* 3 (1910), p. 233.

[5] Liebig, *loc. cit.*

[6] Graham, *Phil. Trans.*, 151 (1861), p. 183; *J. Chem. Soc.*, 15 (1862), p. 216; 17 (1864), p. 318; also "Experimental Researches".

[7] Van Bemmelen, *loc. cit.*

[8] Willard Gibbs, "Scientific Papers," Vol. I.

[9] Thomson, J. J., "Applications of Dynamics to Physics and Chemistry".

[10] Freundlich, *loc. cit.*

[11] Ostwald, Wo., "Colloid Chemistry," tr. by M. H. Fischer, 1919.

[12] Baumann and Gully, *Naturw. Zeit. Land. u. Forst.*, **6** (1908), p. 1; *Mitt. der k. Bayr. Moorkultur-Anstalt* (1910), p. 113.

1910, and in a somewhat modified form and under the name of selective adsorption to soil interchanges in general by Cameron,[1] and Parker,[2] and Harris[3] in America, by Wiegner[4] in Germany and in this country by Russell and Prescott[5] to explain the absorption of phosphates. There are difficulties in the way of such an explanation, and a short account of the development of the theory is necessary. Willard Gibbs and subsequently Thomson pointed out that if a solute lowers the surface tension of a solution it will tend to accumulate in the surface layer. We then get

$$\Gamma = -\frac{C}{RT} \cdot \frac{d\sigma}{dC}$$

in which Γ = the excess concentration in the surface layer, C = the bulk concentration and $\frac{d\sigma}{dC}$ = the differential coefficient of the function connecting σ (the surface tension) with C. This equation applies strictly only to non-electrolytes with no electric charge, and experimental verification has proved difficult as indicated by the work of Lewis[6] and of Donnan and Barker.[7] In applying the theory to electrolytes the earlier electrical double layer hypothesis of Helmholtz[8] has been extended to explain contact potentials in solutions. This was followed by the experimental work of Palmaer[9] and of S. W. J. Smith,[10] which brought out the specific effect of ions in altering surface tension quite apart from the electrical effects, and van Laar by taking these effects into account has brought Helmholtz's calculations into agreement with the results of Smith. Here we have arrived definitely at the idea of selective ion adsorption, and an attempt has been made by Lewis to introduce this modification into the original Gibbs-Thomson equation which then becomes

$$\Gamma = \Gamma_{\text{salt}} + \Gamma_a + \Gamma_b = -\frac{C}{RT}\left[\frac{d\sigma}{dC} + (a + b)\frac{d\sigma}{dV}\right]$$

in which V = the potential difference across the double layer and a and b are the electro-chemical equivalents of the negative and positive ions respectively. At maximum σ no ionic adsorption could occur, and we are left in such a case with the ordinary Gibbs-Thomson equation. Here we are definitely getting away from the original idea of adsorption as being a pure surface tension effect, and we have to distinguish between mechanical and electro-capillary adsorption.

Further, adsorption—whether mechanical or electro-capillary—is an essentially reversible phenomenon. Many reactions often regarded as adsorptions are irreversible, such as those involved in the processes of dyeing and of the filter bed. Such anomalous adsorptions have been studied by various workers, notably by Lewis,[11] Freundlich and Losev,[12] Ramsden,[13] Metcalfe,[14] and Shorter.[1] Some form of colloidal precipitation or gelatinisation involving the separation of a new solid phase evidently occurs since overstepping of the solubility limit does not appear to be essential. In all such cases one can hardly regard the reaction as a mere adsorption : adsorption may occur, but only to be succeeded by some type of fixation. Adsorption in such cases may be regarded as a means of hastening a reaction or of bringing about the conditions necessary for the reaction—chemical or physical—to take place.

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[1] Cameron, *J. Phys. Chem.*, **14** (1910), pp. 320, 393; "The Soil Solution" (Easton, Pa.), 1911.

[2] Parker, *loc. cit.*

[3] Harris, *Mich. Exp. Sta. Tech. Bull.*, **19** (1914); *J. Phys. Chem.*, **18** (1914), p. 355, and **21** (1917), p. 454.

[4] Wiegner, *J. für Landw.*, **60** (1912), pp. 111, 197.

[5] Russell and Prescott, *loc. cit.*

[6] Lewis, *Phil. Mag.*, **15** [6], 1908, p. 499; **17** [6], 1909, p. 466.

[7] Donnan and Barker, *Proc. Roy. Soc.*, **85** A, 1911, p. 557.

[8] Helmholtz, *Wied. Ann.*, **7** (1879), p. 337.

[9] Palmaer, *Zeit. f. phys. Chem.*, **59** (1907), p. 129.

[10] Smith and Moss, *Phil. Mag.*, **15** [6], 1908, p. 478.

[11] Lewis, *loc. cit.*

[12] Freundlich and Losev, *Zeit. f. phys. Chem.*, **59** (1907), p. 284.

[13] Ramsden, *Proc. Roy. Soc.*, **72** (1903), p. 156; *Zeit. f. phys. Chem.*, **47** (1904), p. 342.

[14] Metcalfe, *ibid.*, **52** (1905), p. 1.

The Gibbs-Thomson theory is a special case of the general principle that the energy content of a system tends always to decrease. To include all cases of apparent adsorption Wo. Ostwald[2] has generalised the Gibbs theorem thus : increase of concentration at a surface will always occur when the potential of any form of energy at this surface can be diminished by the process. " Any form of energy " includes of course not only surface tension but also electrical, thermal, and other physical and chemical changes. Thus in some cases solid solution involving slow diffusion into the solid phase may follow the initial adsorption, and the degree of adsorption may be affected by the chemical configuration of the bodies concerned as in the relation of enzymes to optically active substrates and possibly other cases of specificity.

This generalisation of Ostwald is wide enough to cover not only all cases of so-called adsorption, both anomalous and otherwise, but many other physical and chemical processes as well, and in its enunciation we have got very far from the original conception of Gibbs and Thomson.

In investigating so-called adsorptions experimentally the relation between the amount adsorbed and the final concentration of the solution is usually determined owing to the formidable difficulty in the way of the Gibbs-Thomson equation. Several empirical formulæ have been put forward to express this relationship, notably by Schmidt,[3] and by Freundlich,[4] of which the latter is now almost universally employed. This equation

$$\frac{y}{m} = kC^{\frac{1}{p}}$$

is the equation of a curve parabolic in form, and implies that no maximum adsorption is possible as this is always proportional to the pth root of the concentration. It applies with a fair degree of accuracy to many adsorptions but also to many reactions that are not adsorptions. Moreover, it does not apply to some reactions that are considered by some to be adsorptions. Thus adsorption frequently tends to reach a maximum so that beyond a certain concentration no more adsorption will occur. The potash results of Peters[5] are of this type, and the Freundlich equation does not apply to them. Generally p is between 2 and 3, but with many dyes and colloidal electrolytes it may be as high as 9 or 10. It is important to note that since the equation is empirical there is no logical limit to the possible values of p, and in Russell and Prescott's[6] work alone it varied between 1·5 and 8·6. When $\frac{1}{p} = 1$ the absorption is proportional to the concentration, and we get $\frac{y}{m} = kC$ an equation which applies to some cases of anomalous absorption, and also to the distribution of a solute between two immiscible solvents such as iodine between water and carbon tetrachloride. If $\frac{1}{p} = 0$ we have $\frac{y}{m} = k$ and the curve becomes a straight line parallel to the axis of abscissæ. Such a curve applies to an ordinary chemical precipitation such as that of AgCl when $AgNO_3$ and HCl solutions are mixed. It is interesting that the curve of Peters' potash results is approximating to this type. In the case of ordinary adsorptions $\frac{1}{p}$ lies between 0 and 1, but such a curve will also apply to the distribution of a solute between two immiscible solvents in which the states of aggregation of the solute are different, *e.g.* acetic acid in water and benzene. When $\frac{1}{p}$ is greater than unity then relatively more is adsorbed at the higher concentrations and the curve is convex to the horizontal axis. Finally, various values of $\frac{1}{p}$ may be found for different values of C in the same series, the resulting curve showing maxima or minima or points of inflexion. It is evident, therefore, that the equation is of extraordinarily wide application: even when we restrict the value of p between 2 and 10 it applies to types of phenomena that cannot possibly be related. And yet the shape of the curve is the only criterion of adsorption that is employed in agricultural and much physiological work. As a criterion it is unsound to a degree, and when used as such it is the very prototype of an obscurantist formula, and is harmful in so far as it tends to hide rather than to expose the real nature of the reaction concerned. As a means of characterising a particular type of reaction it is of more than doubtful value, although it may be suggestive when used as an interpolation formula to express certain experimental results. In such cases it would be better to use the word "sorption" as suggested by McBain[1]—a word which emphasises our ignorance of the nature of many of these reactions and which does not commit us to any particular theory. At the same time the equation is so universally employed as an explanation rather than as a mere statement of experimental results that it would be better altogether to avoid its use rather than to run the risk of accepting as an explanation what can at best be regarded as a mere label to denote a group of incompletely classified but not unclassifiable phenomena. This is the more desirable as the facts of absorption by soil are described equally well and explained more satisfactorily by the older chemical theory of Way as modified and developed by Lemberg, Armsby, and Sullivan.

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[1] Shorter, *Phil. Mag.*, **11** [6], 1906, p. 317 ; **17** [6], 1909, p. 560.

[2] Ostwald, Wo., *loc. cit.*

[3] Schmidt, *Zeit. f. phys. Chem.*, **15** (1894), p. 56.

[4] Freundlich, *loc. cit.* [5] Peters, *loc. cit.* [6] Russell and Prescott, *loc. cit.*

[1] McBain, *Phil. Mag.*, 18 [6], 1909, p. 916.

SOIL ACIDITY IN ITS PHYSICO-CHEMICAL ASPECTS.

BY E. M. CROWTHER, M.SC., A.I.C., ROTHAMSTED EXPERIMENTAL STATION.

The application of basic materials, such as lime or chalk, has long been known to result in increased soil fertility, especially in the case of the so-called "sour soils". Such soils are recognised in practice by a fairly characteristic weed flora, the failure of leguminous crops, and the liability of cruciferous crops to certain fungoid diseases. Sour soils redden blue litmus paper when it is pressed on to the moist soil, so that the obvious view was advanced that the infertility is due to the presence of acids, which are neutralised by the application of lime. Methods for the determination of the amount of this acidity and therefore of the "lime requirement" of the soil, were devised on the assumption that the interaction between a sour soil and a base was a simple neutralisation. Examples of such methods are the Veitch method involving the addition of lime water in slight excess, and the Hutchinson-McLennan method in which the $CaCO_3$ removed from a calcium bicarbonate solution is estimated.

A second group of methods depended on the curious fact that sour soils set free considerable amounts of titratable acid from salt solutions such as KCl or $KC_2H_3O_2$.

A large amount of work has been devoted to the investigation of the validity of these lime requirement methods. Several of them have provided quite useful practical information, but their application is circumscribed by the fact that it is only on comparable soils that the "lime requirements" adequately represent the response to liming. Further, all the methods are very sensitive to slight variation in technique, and different methods give widely divergent results when applied to the same soil. In a recent study of the Hutchinson-McLennan method, Fisher has shown that the amount of $CaCO_3$ removed from solution is not independent of the concentration of the bicarbonate used, but that the distribution of $CaCO_3$ between soil and solution may be represented by the usual adsorption equation. The taking-up of base by a sour soil appears to involve not only the simple neutralisation of acids, but also some absorptive process by the soil colloids.

Many workers have attached more importance to the absorption than to the presence of acids. It has been held that in fertile soils, well provided with reserves of $CaCO_3$, the absorptive power of the soil colloids for bases is fully satisfied, but that the continuous removal of basic material by plant growth and drainage may result ultimately in a colloidal system with a marked affinity for bases. Ramann therefore replaced the term "acid" as applied to soils by "adsorptively unsaturated". Baumann and Gully working with peat soils and Cameron and Harris with mineral soils denied the existence of acids in soils giving aqueous extracts neutral to litmus paper. Selective adsorption of bases was held to account not only for the action of litmus paper and for the liberation of acid from salt solutions, but for the large variations in the amounts of different bases taken up by the soil from alkaline or neutral solutions. The possibility of establishing the existence of acids in the soil by titration was the subject of prolonged controversy. Truog, for example, maintained that by using dilute solutions to reduce side-reactions, equivalent amounts of NaOH, $Ca(OH)_2$ and $Ba(OH)_2$ were neutralised by sour soils.

THE MEASUREMENT OF THE H˙-CONCENTRATION OF SOILS.

The lime requirement methods were intended to measure the "quantity factor" of acidity, *i.e.* the total amount of acid as measured by titration. But the acid properties of a solution can only be expressed by the "intensity factor," *i.e.* the hydrogen ion concentration (or activity). Many sour soils have been shown to possess a H˙-concentration considerably greater than that of water, so that there is now no valid reason for denying the existence of acid substances in sour soils.

The use of the hydrogen electrode is practicable in complex mixtures only if they possess considerable buffer action, *i.e.* some mechanism for maintaining an almost unchanged reaction on the addition of small quantities of acid or alkali. Aqueous extracts of soils are but feebly buffered; the introduction of a little alkali, such as the ammonia produced by the reduction of nitrates by the hydrogen electrode, causes considerable alteration in reaction. Suspensions of soil in water, however, are strongly buffered and give quite definite results with the hydrogen electrode. A very wide range of H˙-concentrations has been recorded; thus Gillespie found values for $-\log [H^{\cdot}]$ or pH from 4·4 to 8·6. Sharp and Hoagland with a somewhat less satisfactory technique found a range of 3·7 to 9·3, though the fertile soils examined by them showed very similar values varying from the neutral point 7·0 to about 7·5 on the alkaline side.

The potential difference which forms the basis of the method can be measured with a high degree of accuracy, but with soils difficulties are introduced by the necessity of working with suspensions. Measurements cannot be made on soils at their natural water or CO_2 contents. In well-buffered mixtures dilution produces little alteration in reaction, and it has been found that variation in the soil-water ratios or the addition of moderate quantities of CO_2 to the hydrogen used, produces but little alteration in the results obtained. It is therefore generally assumed that the values obtained approximate to those of the soil solution.

The sulphone phthalein indicators of Clark and Lubs have been used for the determination of the H˙-concentration of aqueous soil extracts, and, in the only comparison hitherto made with the results for soil suspensions by the hydrogen electrode, Gillespie has obtained very satisfactory agreement. This is especially important because the most probable sources of error in the two methods arise from different causes. The principal difficulty involved is the preparation of sufficiently clear soil extracts for colour matching. Prolonged centrifuging is often insufficient and it is then necessary to resort to dilution, since filtration or flocculation often produces quite marked changes in such weakly buffered solutions.

Considerable importance has been attached in the past to the differences towards litmus paper exhibited by the moist soil and the soil extract. An insensitive indicator such as litmus, especially on paper, requires an appreciable amount of acid to effect the change to red. With small quantities of weakly buffered solutions, such as soil extracts or very dilute HCl, the reaction of the liquid may be seriously changed, whilst if a large bulk of solution be left in contact with the litmus, leaching may occur before the correct tint is reached. When the paper is pressed on to the moist soil, the proximity of the soil allows rapid diffusion of acid to the paper, whilst its reaction is changing, and a fair indication of the soil reaction may be obtained.

The mechanism of buffer action in the case of partially neutralised weak acids is easily explained in terms of the dissociation constant, but it is not generally possible to analyse the factors involved in more complex systems. The difficulties of technique have prevented much work on the determination of the changes in $-\log [H^{\cdot}]$ during the titration of acid soils with bases, but it has been found that the soils are well-buffered over considerable ranges of $H^{\cdot}$-concentration. In other words the titration curves showing $-\log [H^{\cdot}]$ as a function of the amount of base added are practically linear without any sharp breaks corresponding to "end points". The slopes of the curves vary considerably from soil to soil, so that it is possible for a strongly acid soil to possess little titratable acidity or a low lime requirement, whilst neutral or even slightly alkaline soils may show an appreciable lime requirement if the soil be brought into equilibrium with an alkaline solution.

ACTION OF NEUTRAL SALTS ON ACID SOILS.

Sharp and Hoagland have shown that $BaCl_2$, KCl or NaCl increase the $H^{\cdot}$-concentration of suspensions of acid soils. In a more detailed study of the action of salts on humus suspensions Gillespie found that the same action occurs and that the increases produced by different chlorides are in the order Ba>Na>K. The interpretation of these results is complicated by the fact that these salts produce similar, though smaller, increases in the $H^{\cdot}$-concentration (or activity) of true solutions.

The increase in $H^{\cdot}$-concentration is accompanied by considerable amounts of titratable acid, the estimation of which was used in some of the early lime requirement methods. In spite of much investigation, the interpretation of this action is still obscure. On the selective adsorption theory the action is regarded as strictly analogous to the liberation of acid and fixing of base during the precipitation of colloidal solutions of As_2S_3 by $BaCl_2$. The importance attached to the adsorption of cations for the coagulation of negative colloids gave some support to this view, but no clear mechanism was advanced to explain the liberation of acid.

Neutral salt extracts of acid soils contain weak bases—chiefly Al, though Fe, Mn or even Zn are sometimes found—in amounts roughly equivalent to the titratable acidity. Parker modified the selective adsorption view by assuming that the salt is hydrolysed, the base being adsorbed whilst the acid dissolves the weak bases from the soil. Others regard the aluminium salts as the cause rather than the result of the acidity of the neutral salt extracts. Rice found that the relations between the $H^{\cdot}$-concentration and titratable acid of KNO_3 extracts corresponded closely with those of mixtures of $Al(NO_3)_3$ and KNO_3 and concluded that the amount of aluminium was precisely equivalent to the titratable acid, the apparent exceptions arising from the difficulties of analysis and titration. Rice ~~and~~ Daikuhara regard this basic exchange as taking place with loose adsorption compounds of weak bases which characterise acid soils, whilst Veitch and other later workers hold that the interaction occurs with the complex alumino-silicates of the soil. Whatever the mechanism of this basic exchange, the differences in the hydrolysis and solubilities of the various salts concerned will account for many of the results. The excess of a salt of a weak acid prevents any considerable rise in H$^{\cdot}$-concentration, so that the aluminium salts are almost completely hydrolysed and precipitated with the liberation of much-titratable acid, whilst with salts of strong acids higher H$^{\cdot}$-concentrations occur, so that the Al remains in solution and the reaction soon reaches an equilibrium point. Similar reactions of the aluminates and silicates of Ca or K will account for the greater "adsorption" of Ca during the action of the hydroxides on sour soils. In the case of peat soils Sven Odén suggests that the acidity of salt extracts arises from the displacement of small amounts of organic acids adsorbed by humus. He found no HCl by distillation of a KCl extract of an acid peat, and an aqueous extract of the treated peat was not alkaline, so that there was no evidence of any hydrolytic decomposition by adsorption.

The complexity of the soil system is such that nothing is to be gained at present by formulating any general theory of the origin and nature of soil acidity.

RELATION OF SOIL ACIDITY TO PLANT GROWTH.

Until recently soil acidity has been regarded as a pathological condition to be avoided by liming, but the reaction of the soil may vary within fairly wide limits and it does not follow that $-\log(H^{\cdot}) = 7{\cdot}07$ is the optimum for plant growth. Soil fertility is the resultant of the interaction of a large number of factors on the plant, and these factors are likely to be influenced to different degrees by the reaction of the soil solution. There is evidence that a distinctly acid reaction may be desirable for certain crops, and attempts are being made in New Jersey to increase the acidity of potato soils by the production of H_2SO_4 through the oxidation of sulphur added to the soil.

The reaction of acid soils is frequently of the same order as that of plant roots, so that the infertility of most acid soils would not appear to be due to the direct action of the acid on the roots. Of the indirect effects Truog attaches the greatest importance to the lack of available basic material, such as $CaCO_3$, for the neutralisation of the acids produced in the plant, whilst several workers have ascribed the infertility to the toxic action of aluminium compounds. Gillespie has recently made some preliminary measurements of the reduction potentials of water-logged soils, and has suggested that the "sourness" of poorly drained soils may be the result of their high reducing power. ✓

An extensive bibliography of soil acidity is given by E. A. Fisher, *Journal of Agric. Science*, **11** (1921), p. 19.

THE FORMATION OF PANS IN SOIL.

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The existence of a pan in a soil where such is not on the surface means the confinement of the roots of the crop plants to a comparatively shallow layer, and the consequent unsatisfactory development of the plant. This may be brought about either by the inability of the crop to obtain the water that it requires, or by the failure of the food supply in the case of crops which make a heavy demand upon a soil.

The pan layer itself consists of a more or less sharply defined band of material where the gradual transition from the surface to the underground soil is broken. The characteristics of this layer are a large diminution in the pore space of the soil which slows down and may in extreme cases completely stop the movements of air and water in the soil, and which consequently does not allow plant roots to pass through it.

The concentration of the soil into such a layer may be of two kinds; it may be caused by the compacting which is produced by the continued passage of heavy instruments of tillage to a given depth, or it may be caused by the removal of material either in the form of colloid soils or in the state of solution, and its deposition at lower depths in the soil where it acts as a cementing material to the normal soil particles.

A pan of the first kind which is that known in this country as a plough pan seems to owe its origin to long continued cultivation to a given depth, and the consequent compacting of the layer immediately underneath. The washing down of fine particles and the removal of colloid substances from the surface will all tend to make this layer become more and more impervious. It is apparent that any method of cultivation which tends to destroy the aggregate structure of the soil or to produce deflocculation will act in the direction of intensifying the impervious character of this layer. From the method of its origin it is obvious that a pan of this description is confined to land under cultivation or land which has been cultivated at one time or another.

There exists, however, in certain parts of this country and in many other districts of North-Western Europe another type of pan formation which is confined to land that is carrying or has lately carried a heath vegetation or a forest crop. Pan formation of this nature is nearly always confined to soil composed for the most part of quartz sand, and where it occurs on soils of a heavier type its character and origin appear to be slightly different.

In the case of the formation of pan on the sandier type of soil, owing to the rapidity of normal drainage in such land, the existence of the impervious layer is very marked.

A soil profile will show four distinct layers:—

1. A layer of decaying vegetation.
2. Sand of a peculiar greyish-brown colour.
3. Black or brown or red hard layer.
4. Unaltered sand.

The pan layer which occurs at different depths varies in colour from a dark brown to a reddish-yellow. It is hard and difficult to break in the case of those of a red and yellow colour, but very markedly less so in those of a brown colour. Exposure to air causes it to disintegrate and fall to pieces comparatively rapidly.

An analysis of the layer shows it to contain almost invariably a high percentage of organic matter, and to consist very largely of the original sand cemented together by organic matter and certain other substances. The subsoil appears to be the ordinary and typical sand of the locality unaltered in any way. The zone immediately above the pan contains a certain small amount of organic matter which on removal leaves a sand almost devoid of colouring matter from which quite clearly most of the iron has been removed. On the surface occurs a layer of heath vegetation or the leaf layer of a forest soil, where the decomposition of the organic material is slow, and where a humus of an acid character is produced. A necessary condition for the formation of this pan deposit appears to be the almost total absence of calcium carbonate. This and the presence of an acid humus layer on the surface are the determining conditions.

Analyses of the various sand layers invariably show an almost entire removal of all soluble material from the grey sand, this being especially noticeable in the case of alumina, ferric oxide, and silica. Plant food substances such as potash and phosphorous pentoxide show a similar though smaller exhaustion. This means that this zone is an extremely poor one from the point of view of plant nutrition so that the confinement of the roots of plants to it is specially disastrous. This removed material is concentrated in the pan layer so that its content in the above mentioned substances is larger than in the underground sand. It thus appears that the formation of the pan is connected with the existence of a layer of acid humus on the surface, and is produced by the removal of mineral material from the surface soil and the precipitation of it at lower depths in the soil together with humus, both forming the binding material of the sand.

The problems connected with soil formations of this kind may be grouped under two headings:—

(*a*) The removal of material from the layer which becomes bleached.

(*b*) The accumulation of it to form the pan proper.

The rate at which organic matter decomposes has an undoubted effect upon the characters of the humus produced as has also the content of the soil in soluble material, particularly in calcium salts. The fact that this particular formation is of much commoner occurrence upon soil containing much quartz of large size is important in this connection. The first effect of the production of humus would be the rapid removal of soluble substances from the surface layers of the soil—primarily calcium carbonate. Analyses of the layers show with great regularity a higher content in calcium at the lower depths. With the removal of such substances there will come a time when the conditions become more favourable for the migration of the soil colloids.

Up to this point the content of the soil in calcium and other soluble substances has prevented such colloids as are present from assuming the sol form. From this point onwards, however, the humus itself and by its stabilising effect such inorganic colloids as ferric hydroxide and aluminium hydroxide will be more and more liable to removal from the surface downwards.

In addition to the removal of iron and aluminium and other substances from the surface layers there will also be a tendency in consideration of the very low concentration of electrolytes in the solution for the destruction of aggregate structure and for the actual removal of fine silicate particles, the finest portions of clay to the lower depths.

The variation in the silica-alumina ratio which is observed at varying depths suggests this is not of great importance, so that in those soils where iron pan is of the commonest occurrence it may not be the cause, whereas in heavier soils where any marked pan occurs it would seem to be the determining factor.

It has been held that pan formation was due to reduction of ferric compounds by the humus, and their subsequent removal as ferrous bicarbonate and oxidation and precipitation at lower levels in the soil. This might be true if the concentration of iron was the main feature of the pan, but the concentration of humus is even more characteristic.

The explanation that removal of iron and formation of pan is caused by the formation and oxidation of iron humus compounds is made difficult because of the fact that in some cases the concentration of iron in the pan is not marked while that of alumina always is.

The removal of material depends on:—

(*a*) The formation of an acid humus layer.

(*b*) The removal of soluble substances, especially calcium, from the layer beneath.

(*c*) The tendency for the production of humus sols.

(*d*) The protective action of these upon the inorganic colloids present. Ferric and aluminium hydroxides and silicic acid.

(*e*) The protective action of these upon the silicate particles, and the tendency to destruction of aggregate structure.

The deposition of these removed materials at a certain depth in the soil which varies with local conditions is not easy to account for.

If the above explanation of the nature of their removal is true the pan formation should be due to the coagulation of these sols. There is evidence to show that the amount of calcium carbonate increases with depth, that at any rate calcium increases with depth, and that this increase in concentration together with the greater amount of weathering proceeding at this depth causes such a concentration of electrolytes as to cause coagulation, first of the humus and then of the other colloids. Against this view it must be remembered that as far as we have information these humus colloids seem very stable and are not very sensitive to electrolytes, even in the presence of divalent ions. Dessication in part makes the change irreversible, and it would appear that this and the subsequent oxidation which may occur is sufficient to account for the commencement of the deposition.

This first layer will act as a filter, and will tend more and more to separate out the removed material. In this way may be produced the beginnings of what becomes later on a pan which will alter and become harder and more resistant the older it gets owing to the oxidation of the humus and the cementing of the sand grains to iron and aluminium hydroxides.

In conclusion, there appears to be no doubt that the separation of removed material into a definite layer as in pan formation is an exceptional rather than a usual feature, but that the removal of these materials and more essential plant food substances such as phosphorus and potassium is always associated more or less with the existence of an acid humus layer. It is in this connection that a more precise knowledge of the physical and chemical changes involved in this reaction is going to be of the greatest benefit to agricultural practice.

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DISCUSSION ON "ADSORPTION PHENOMENA".

Dr. W. R. Ormandy: I should like to say that it seems to me the whole of these papers, like the whole of the discussion, emphasise the point of the desirability of carrying out experiments on clay, in the sense in which the ordinary chemist understands the word clay, and not degraded products which may be of the nature of finely divided carborundum. It is obviously simpler to investigate a problem from the point of view of pure clay rather than from that of a clay mixed with a lot of other things which introduce more unknowns. Incidentally, if the large amount of acid which is set free, for instance when clay is shaken up with succinate of soda, is due to the formation of alumina compounds, which are afterwards hydrolised, and the alumina definitely re-precipitated, so that the acid may become free, then all you have to do is to boil up your soil with some sodium succinate and convert all your kaolinite into free silica and free alumina. It should be very interesting to manufacturers of aluminium as a cheap method of producing alumina directly from clay.

Professor Sven Odén: With regard to adsorption phenomena in soils I think that Mr. Fisher is quite correct when—though for most cases preferring the purely chemical point of view—he says that both types of absorption may occur: base exchange and true adsorption. I have stated, in the case of ammonia reacting with peat soils, that pure chemical salt-formation occurs, but that the ammonium humate thus obtained is partially adsorbed by humus if the latter is in excess.

Also, with mineral soils, I have found that, for example, quaternary Swedish clays (Ancylus and Yoldia clay) react with alkali salt solutions mainly under adsorption, whereas Nile clay from Korashin does not follow any adsorption formula at all, but corresponds to a pure chemical reaction, the nature of which I have not yet been able entirely to grasp.

With regard to Dr. Ormandy's last remark I quite agree with him that we should take up these investigations on a more pure line than soils, but I do not think that even china clay is pure enough; we should begin with pure mineral fragments such as felspar, silica, and mica or even with diamond powder. If Dr. Ormandy can prove that a neutral salt solution, *e.g.* KCl, when shaken with diamond powder, becomes acid or alkaline, I shall abandon my unfavourable opinion of the disintegration theory.

Dr. E. J. Russell: With regard to Dr. Ormandy's suggestion that agriculturists should experiment with clay, could he tell us precisely what is clay? We, as agriculturists, know what we mean when we speak about clay, but how does Dr. Ormandy define the clay taken from 130 ft. below the surface? As agriculturists we are not very interested in what happens 130 ft. down; our concern is with the top 9 or 10 in., and we recognise very marked differences between that layer and mineral materials which are 130 or 140 ft. down. Therefore, I am not very clear in my own mind that we should be much helped by studying pure china clay taken from such depths, and unless we stick to the top 6 ins., we shall get into the realms of artificiality and do a great deal of work on problems that will not help us much.

Mr. Fisher's paper is of very great interest. One is bound to recognise that chemical changes do go on during these absorptions, and he has shown that the adsorption equation used as a criterion of adsorption, and assumed to discriminate roughly between chemical and physical phenomena, affords no reliable means of discrimination, and consequently that some other means must be sought, if, indeed, there is a difference. It is quite possible, however, that no sharp line exists between physical adsorption and chemical combination, and that for molecules of certain size it is very difficult to say whether the attraction between them is chemical or physical. It may be that the absorptions going on in the soil are on the border line: one is dealing with very complex silicates, to which no exact constitution can be given. The great value of Mr. Fisher's paper is that he shows that this adsorption equation, which has been steadily extended in its application to cover first one thing and then another, can, by the exercise of a little ingenuity, be made to fit chemical reactions of the type he has discussed. If we are to make any distinction between chemical reaction and physical adsorption we shall have to find some other criterion.

Mr. B. A. Keen: With regard to Dr. Ormandy's suggestion as to the use of china clay, I did some experiments on the evaporation of water from moist china clay. The water evaporation from a sample of pure china clay was practically identical with that from moist sand.

I am aware that china clay has certain definite properties, but my evaporation experiments show that it does not possess in any degree the characteristic relationships with water, of the colloidal complex present in soil.

Mr. E. A. Fisher replying to the discussion said: Referring to Dr. Russell's remarks that soil interchanges are on the borderline between chemical and physical change, we do get strong similarity between such interchanges and others that are known to be double decompositions, such, *e.g.*, as the reaction between calcium chloride solutions and certain silicates. Such similarities can hardly be accidental, and moreover, many of these undoubted double decompositions can be expressed quite well by the ordinary adsorption equation.

Dr. Russell made the remark in his opening address that we cannot make use of the soil colloids to explain one set of phenomena and put them in our pockets when we want to explain other soil phenomena. This applies equally well to the old-fashioned chemical theory: if, as is known to be the case, there are chemically reactive substances present in the soil, we cannot put these altogether on one side when we want to explain phenomena that it is fashionable to explain from a colloid standpoint. The truth is that the colloid properties are not substitutes for the chemical properties, but are superimposed on the soil in addition to the chemical properties. The tendency, however, in most recent work in this field is to describe the phenomena observed entirely in terms of adsorption. There is, perhaps, nothing very wrong about this if workers were a little less definite in their statements or employed some other criterion of adsorption than an empirical equation; instead of talking of adsorption in this connection they might at least use the term "sorption," for the truncated form of the word does cast a doubt as to the completeness of the supposed explanation. The adsorption equation after all is a mere statement of experimental results. It is not an explanation although many people take it to be such, and it is this interpretation that I personally feel rather strongly about.

SECTION V.—PAPERS AND DISCUSSION ON "COLLOIDAL PHENOMENA".

ON CLAYS AS DISPERSE SYSTEMS.

By Sven Odén.

1. The Definition of Clay.

If one searches the literature of geology and agriculture for a definition of the meaning of the term "clay," one finds a number of attempts to attach the characteristic properties of clay to certain definite substances, which are supposed to be the chief components, and, though more or less impure to be the essential components of the natural clays in all their forms.

As such an essential component the hydrated silicate of aluminium, *Kaolin*, was generally regarded formerly. Kaolin was later replaced by the earthy zeolites. (Th. Way, J. M. van Bemmelen, R. Gans): and more recently by many sorts of soil colloids: colloidal silicic acids, aluminium hydrate, iron oxide, allophane, and so forth (F. Cornu, P. Rohland, H. Stremme, and others).

A view differing in principle was put forward by A. D. Hall.[1] According to him it is not the chemical nature of the substance which characterises clay, but, before everything, the fineness of the constituents. This view was also upheld in principle by A. Atterberg,[2] though he was of the opinion that Muscovite and Biotite were the characteristic minerals in the Swedish quaternary clays.

For the reasons which are set out below I think, in agreement with Hall, that the following definition of clay is in accordance with experimental results: Clays are disperse formations of mineral fragments in which particles of smaller dimensions than 2μ predominate.

Among these mineral fragments, quartz, felspar, mica, and others may occur, as well as their different weathering-products, kaolin, bauxite, hydrargillite, zeolites, allophane (Stremme), gelatinous silicic acid, iron oxide, and so forth, but none of these constituents is necessary to characterise a sedimentary soil as clay. All that is necessary is that the smallest particles preponderate. The limit is at present set, according to Atterberg, at 2μ and one may reckon on more than half of the total amount of particles falling about this limit, but these limits are, of course, only arbitrary, and strata where particles of 2 to 5μ magnitude compose the greater portion, show the transition to sand and silt formations. It is also probable that the limits of magnitude within which the characteristic properties of clay are found are dependent on the chemical properties of the material, and a clay composed chiefly of kaolin and quartz must in all probability be appreciably finer than clay consisting of, for example, biotite and hydrated silicic acid, in order to attain the firmness and plasticity typical of clay. In this connection it may be pointed out that it is not any special chemical colloids which comprise the clay colloids. The true soil-colloids are the innumerable fragments of both weathered and unweathered minerals, crystal chips and amorphous substances, which, in a state of fine division, constitute the clay.

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[1] "The Soil" (London, 1912), pp. 34-39.

[2] A. Atterberg, *Intern. Mitt. f. Bodenkunde*, 1, 7 (1911), 7, 718 (1914); *Kolloidchem. Beih.*, **6**, 55 (1914).

By *colloids* or disperse formations, we understand, in physical chemistry, two-phase systems where the one component, for example, the solid phase (here the mineral grains), occurs in finely divided (disperse) form, and is dispersed in the other component, the dispersion medium (for example, water).

But while, in colloidal solutions and in the majority of cases in gels, the disperse phase constitutes the smaller part of the system (often a few per cent. at the highest), in the clays the disperse phase preponderates, and the dispersion medium (water, or water vapour and air) is only to be regarded as a filling for the interstices between the mineral particles.

The clays also, in contrast to the majority of other colloid systems, consist of grains of all possible sizes, from sand grains of one millimetre to particles of one hundred-thousandth part of a mm. ($0{\cdot}01\mu = 10\mu\mu = 0{\cdot}00001$ mm.). The importance of the percentage distribution of the mineral grains over the different sizes for differentiating and classifying clays will be dealt with further on.

An enormous increase in surface area proceeds hand in hand with this higher subdivision, which subject has been treated in my previous note. This large surface also brings about adsorption of different salts, and even gases, by the particles, which are thereby fixed, and protected against washing out.

But while, according to the reasoning set out above, it is not the chemical nor the mineralogical constitution of the material, but only its state of division, which decides the apparent properties of the clays, the chemical nature of the constituents plays, of course, an important role in the agricultural and technical valuation, and in the more minute characterisation of the different clays. We must here call in the aid of chemico-analytical methods. Against the complete analysis (" Bausch analysis ") of course, no objection can be advanced. It gives us the complete quantitative composition of the clay. But to proceed, as was formerly usual, to call the portion soluble in hydrochloric acid " zeolitic weathered-silicate," and that soluble in concentrated sulphuric acid " kaolin bodies," is misleading. For it is necessary in all extraction methods to take into consideration the degree of fineness of the material. The finer the mineral grains are, so much the more easily are they attacked by acids, and, with the exception of quartz, small mineral particles of all sorts are attacked by hydrochloric acid.[1]

2. THE CHARACTERISATION OF THE CLAYS BY MEANS OF DISTRIBUTION CURVES.

We have seen how the clays are characterised by the fineness of the particles. How shall we now distinguish the degree of this division among the minerals? The answering of this question has been the task of

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[1] P. Zemjatschensky, 11 *Journ. de la confér. de natur. et méd.*, St. Petersbourg, 1901, p. 73; A. Vesterberg, *Intern. Mitt. f. Bodenkunde*, **5**, 37 (1915); S. Odén and A. Reuterskiöld, *Bull. of the Geol. Inst. of Upsala*, **16**, 148 (1919); *Intern. Mitt. f. Bodenkunde*, **10**, 343 (1920).

mechanical soil-analysis, the object of which is to divide up the soil-strata in fractions according to the size of the particles, and to determine the weight of these fractions. But this grading must, for practical reasons, be limited to the isolation of a fairly limited number of fractions, and, as the soil-strata contain particles from the size of sand grains a millimetre large down to amicrons, a classification limited in this way to certain groups of particles is always very imperfect. Two soils might give almost identical figures in such a mechanical analysis and yet be very different with regard to the nature of the grains. This is probably the chief reason why classifications grounded on mechanical soil analysis have regularly failed in their object, and must be abandoned. Mechanical soil analysis calls all particles under 2μ clay. Since it is just these smallest particles which are characteristic of clay, but which, in different clays, may have quite different degrees of smallness, we must lay the greatest stress on the characterisation of just these smallest particles. One might now take into consideration the colloid-chemical methods worked out by Zsigmondy, which consist in counting the number of particles in a limited volume of a suspension of known concentration, but even such methods of procedure are incomplete, for they give a figure only for the mean of the magnitudes of the particles, and these values are often far from the real size of the most numerous particles.[1]

A determination of the distribution, that is to say, of the weight or the number of particles corresponding to each size, here shows itself to be very desirable.

Before entering upon this problem we shall first clearly decide what may conveniently be meant by the term "dimensions," applied to such small mineral particles as these, for to give the length, breadth, and height of all the different mineral fragments is manifestly impossible.

In practice the particles are studied in contact with water, and for this reason I have previously in another place[2] proposed that the "effective radius" of a particle should be defined as the radius of an imaginary sphere of the same material which would sink in water with the same velocity as the particle in question. The detailed argument for this, as well as the laws governing such motions of small particles in a liquid were set out in the same paper.

It was probably Maxwell who first used distribution curves to characterise physical systems, as, for example, to demonstrate the different velocities of the molecules in a gas. The use of the same procedure for soil layers presumes that it is possible to express the number of the particles graphically as a continuous function of the effective radius. This is most easily illustrated by means of a few examples.

If we consider a clay composed of particles of the size of 1μ, 2μ, 3μ, . . . 100μ, as well as of particles less than 1μ, we may express the mass of particles $< 1\mu$, 1μ to 2μ, 2μ to 3μ, and so forth, in percent. of the whole. Such a set of figures would have the same meaning as the results of an ordinary mechanical soil analysis, with the difference that it would be divided into 100 groups, instead of the 3 or 5 of the soil analysis. But to make the figures more easily comprehensible it is more convenient to set them out graphically. This may be done in several ways.

In Fig. 1, are set out as abscissæ the effective radii, and as ordinates a value $q(r)$, which indicates the percentage of the sample consisting of particles larger than this effective radius. For the effective radius 0, this value is 100, for effective radius 10μ for example, it is 75, for effective radius 30μ, it is 50. This indicates that 75 per cent. of the sample consists of particles larger than 10μ, 50 per cent. larger than 30μ, and so forth.

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[1] Odén, *Koll. Zeitschr*, **26**, 109 (1920).

[2] *Intern. Mitt. f. Bodenkunde*, **5**, 257 (1915).

Between 0μ and 10μ lie, therefore, 100 − 75 = 25 per cent., and so on. To obtain the percentage between any two abscissæ we, therefore, subtract the ordinate corresponding to the larger effective radius from that corresponding to the smaller, the difference corresponding to the percentage of particles. This graphical function declines therefore from 100 for the smallest particle to 0 for the largest in the sample. If the curve is horizontal it shows that there are no particles at all in this interval.

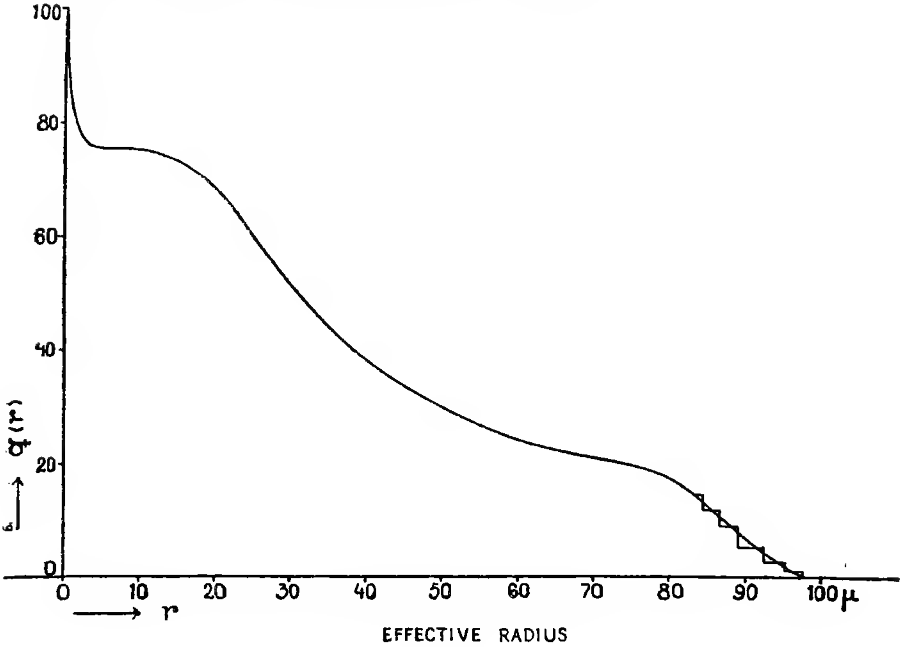

Fig. 1

One entirely theoretical remark may be permitted here. When drawing this curve, if one desires to use a scale such that each particle would be represented, the curve would, strictly speaking, not have this continuity, but would have a step-like appearance such as is represented to the right of Fig. 1, because the number of particles, despite its large amount, is limited, and there must always be size values which have no particles. In reality these intervals of millionths of one per cent. are negligible, and we may give the curve a continuous outline.

The above method of representing the composition of a soil is specially convenient for the treatment of certain problems. In most cases where we wish to get an idea of the numbers of the contents of the different fractions it is better and easier of comprehension to represent the amounts of the particles not as a line but as a surface. This is accomplished by the method shown in Fig. 2, where the effective radius is as before set

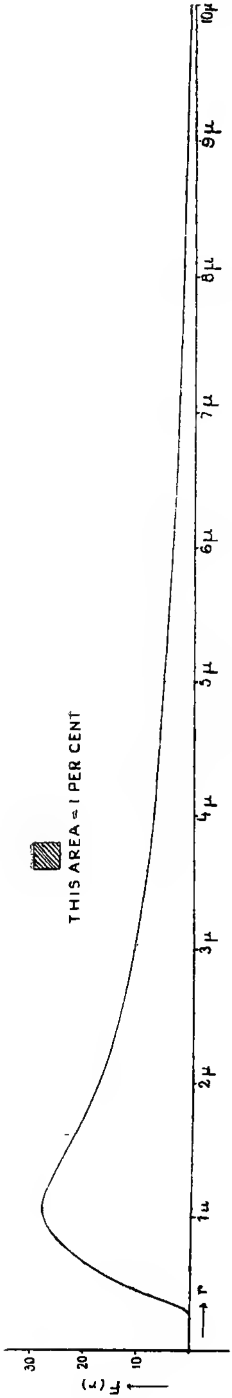
THIS AREA = 1 PER CENT
30
20
10
F(r)
r
1μ
2μ
3μ
4μ
5μ
6μ
7μ
8μ
9μ
10μ

FIG. 2.

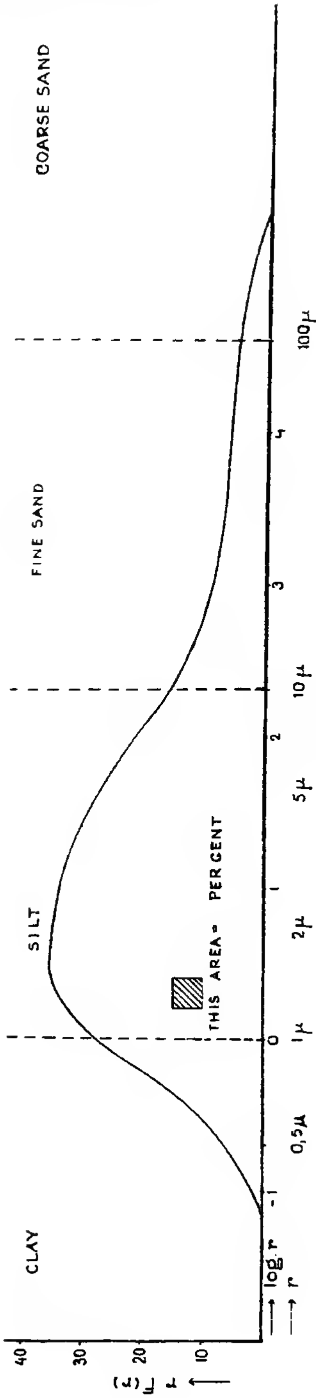
COARSE SAND
FINE SAND
SILT
CLAY
THIS AREA = PER CENT
40
30
20
10
r F(r)
log r
r
-1
0,5μ
0
1μ
2μ
1
5μ
2
10μ
3
4
100μ

FIG. 3.

off as abscissæ, but where we measure as ordinates, a value F(r), such that this value, multiplied by a part of the abscissa axis, gives us a surface which represents the number of particles in the interval of abscissa in question. The number of particles is here represented as an integral, and the number of particles between any two radius-values is obtained simply from the surface encompassed by the axis of abscissa, the corresponding ordinates, and the curve. The easiest way to carry out the graphical representation is to arrange that the total surface comprises 100 units on millimetre-paper, when it is only necessary to reckon the squares for each interval to arrive at the percentage.

If we are considering a typical clay soil, the curve will appear as represented in Fig. 2. If there are, on the contrary, particles of a large range of sizes it would be very inconvenient to use radii as abscissæ, because of the length. If we there use r . F(r) instead of F(r) the surface content is not altered. The curve merely assumes a rather different appearance, and is easier to deal with.[1] *Cf.* Fig. 3.

I have in Fig. 3 drawn lines through 1μ, 10μ, and 100μ, since according to Atterberg's[2] researches these limits are the most convenient to characterise the groups clay, silt, fine sand, and coarse sand.

A soil-layer is therefore a clay, a silt, or a sand soil according to whether the greatest part falls within the limits for clay, loam, or sand.

The properties of firmness, plasticity, and permeability to water, etc., are nevertheless not dependent only on the preponderating constituent and its fineness, but also on substances occurrent to a smaller extent, and therefore greatly dependent on the nature and character of the distribution curve.

As we have seen, distribution curves characterise the loose soils far better than the results obtained by mechanical soil analysis. The determination of these curves may be carried out by carefully levigating a clay in water, and then studying the rate of sedimentation. This may be accomplished by suspending a fine plate from a balance beam immediately over the bottom of the sedimentation vessel, and from time to time determining the weight of the deposited particles. The rate of accumulation of these particles is dependent at every moment both on the number of the particles and their weight and distribution, and this may be calculated therefrom.

Before going into this the experimental method may be sketched briefly.

3. THE METHOD OF EXPERIMENT.

The experimental method is based, as before mentioned, on the suspension of a metal plate A, over the bottom of the vessel in which the sedimentation is carried out. The plate is suspended by fine gold wire from the balance B, which allows the sediment to be weighed continually.

It is not necessary that the plate should be as large as the real bottom of the sedimentation vessel, but it may simply be regarded as the base of a cylinder whose height h is identical with the distance from the plate to the surface of the liquid. The remaining parts of the suspension nearer the sides of the vessel may be disregarded, if we reckon all weight determinations in percentage of the total weight P∞ after all the particles have finally subsided.

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[1] Since $d(lnr) \,.\, rF(r) = \frac{1}{r} \,.\, dr \,.\, rF(r) = drF(r)$.

[2] A. Atterberg, *Intern. Mitt. f. Bodenkunde*, 1, 7 (1911), 7, 718 (1914); *Kolloid chem. Beih.*, 6, 55 (1914).

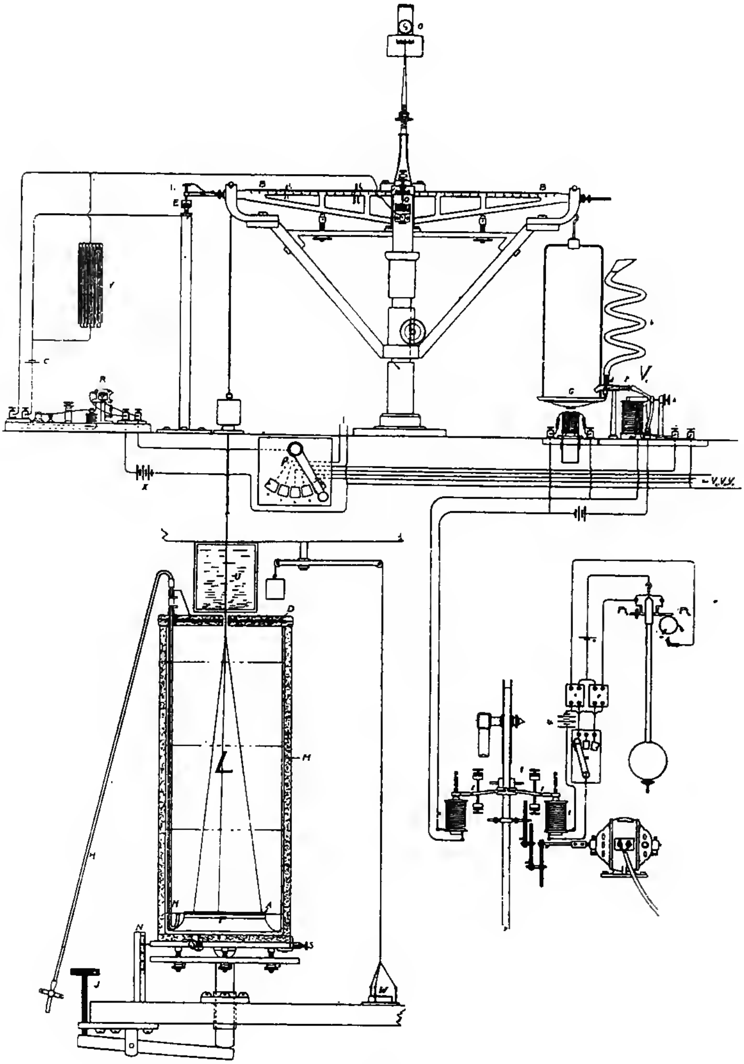

FIG. 4.

If the balance is adjusted at the beginning to equilibrium, and a weight[1] *d* is afterwards placed on the balance pan G and the sediment allowed to deposit on the plate until this weight is counterpoised, then the balance swings to the left, making the electric contact at E, which causes the time to be marked on the telegraph tape by the apparatus RC*nl*, and further causes the automatic feed V to introduce another weight on to the balance pan G. This breaks the contact at E until equilibrium is again attained, and the weight of 2*g* is reached, when the time is again marked.

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[1] Steel balls of the weights of (*b*) 0·1276 g. (*c*) 0·0544 g. (*d*) 0·0153 g. were used for weights.

The times corresponding to equilibrium may be read off at leisure by means of the apparatus—also electric—from the clock P*t*. *rtl*, which marks seconds or minutes on the telegraph tape.

By raising the stop and properly adjusting the contact at E we may bring the right and left positions of the balance very near to each other, and also to the equilibrium position, and so avoid unnecessary oscillations in the liquid.

I have in another place[1] described in detail the experimental arrangements, and the best way of recording the results. It suffices to mention here that all the experiments were carried out in a constant-temperature room without heating arrangements, and that generally the variation of temperature per day did not exceed 0·1 to 0·2 deg. C., and consequently no special measures to compensate for varying weight of the plate due to changed specific gravity were taken. And further, that both Th. Schloesing *père*[2] and I have shown, by purely experimental methods, that, provided that the suspension be not too concentrated, the path of the falls of the individual particles may be regarded as being relatively uninfluenced by those of the others; in other words, that the accumulation curve, after correction to a certain normal height, 10 cm.,[3] and to percentage of the final weight, is *relatively* independent of both the absolute height of fall and the total weight of the levigated substance.

Theoretically, of course, in this case, the conditions necessary to the application of Stoke's law are not experimentally fulfilled, but if we avoid concentrations over 1 per cent. we may in practice assume that the particles fall independently of each other.

The recording was not usually continued for longer than 100 hours. The whole of the sediment had, of course, seldom fallen in this period, but, since it was necessary to determine $P\infty$, at the end of this period the remaining liquid was carefully drawn off through the syphon *h*, from the height of the plate, and a new determination made with half of this after addition of a coagulator, whereby the weight of the undeposited residue was determined. The sum of the final weight in experiment 1 and twice the weight found in experiment 2 then give us $P\infty$. In the other half the mean size of particle was determined ultramicroscopically, according to Zsigmondy-Siedentopf.

Let us regard the particles as spheres of specific gravity S and call the effective radius *r*. If we optically delimit a small volume, v cm.^{3}, of the diluted clay suspension, we may, if p be the concentration of the disperse phase in gm./cm.^{3} and n the number of particles in the volume v, calculate the radius from the equation

$$r = \sqrt[3]{\frac{3}{4\pi} \times \frac{v \cdot p}{s \cdot n}} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The specific gravity is always taken as 2·7, v is expressed here in cub. cm.

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[1] *Bull. of the Geol. Institut.*, Upsala, **16**, 15 (1918).

[2] Th. Schloesing *père*, *Compt. rend. de l'Acad.*, Paris, **136**, 1608 (1903).

[3] For a fall of 5 cm., it is therefore necessary to multiply the time by 2, for 20 cm. fall, by 0·5, and so on, since the rate of fall is inversely proportional to the height of fall *h*.

4. Calculation of the Distribution Curve from the Accumulation Curve.

In the following, by *distribution curve* is indicated the function F(r), which gives the relation between percentage weights of the suspended material and the corresponding radii, by *accumulation curve* P(t), the weight of sediment (weighed in water) as a function of the time. If P_1, P_2, P_3, be the weights corresponding to the times t_1, t_2, t_3, we may, for a small interval, write:—

$$\frac{P_2 - P_1}{t_2 - t_1} = \frac{dP(t)}{dt}.$$

The different values of the angle coefficient, or, in some cases, more conveniently the logarithm of the angle coefficient, of this accumulation curve at different times as a function of the time (or logarithm of the time), is designated *the auxiliary curve*, and by means of this it is possible to determine graphically the other derivatives of the accumulation curve.

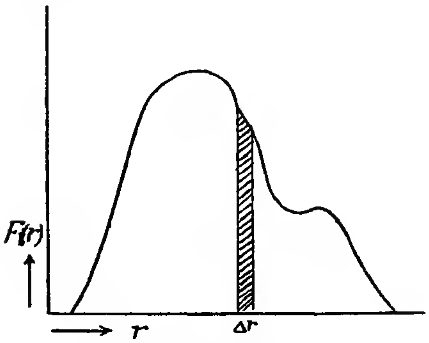

Fig. 6.—Distribution Curve.

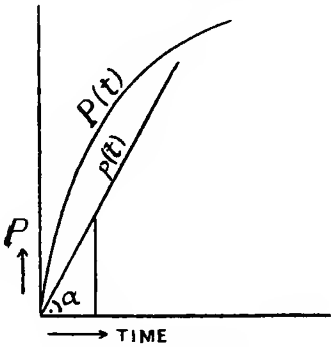

Fig. 7.—Accumulation Curve.

Let us first consider the simplest case, where all the particles have the same effective radii and are similarly distributed in the liquid, and let p be the amount deposited as a function of the time. The accumulation must then proceed at a rate proportional to the rate of fall v of the particles, and to the concentration c. The latter can, if the total amount of the particles after complete deposition = A, the area of the bottom of the sedimentation cylinder = 1, and the height of fall = h, be written $c = \frac{A}{h}$.

The rate of accumulation then becomes $\frac{dp}{dt} = \frac{A \cdot v}{h}$. Const.

If p be here expressed as a fraction of A, and v be given in terms of the same units as t and h, this constant = 1.

The weight of deposited sediment (Fig. 7), p, after a certain time, t, is therefore clearly

$$p = t \cdot tg\alpha = t\frac{dp}{dt} = t\frac{A \cdot v}{h} \quad . \quad . \quad . \quad (2)$$

This equation holds good, however, only so long as there are any falling particles in the fluid, that is to say, until p = A. This time during which the equation holds is clearly the same as that which the topmost particle requires to reach the bottom, and is obtained by writing in equation (2), p = A.

$$t = <\frac{h}{v} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (3)$$

and the effective radius corresponding to this time is found from Stokes' formula solved with regard to r.

$$r = \sqrt{\frac{h}{Ct}} \quad . \quad . \quad . \quad . \quad . \quad . \qquad (4)$$

This effective radius corresponding to a certain fixed time of fall, t, is in the following designated ρ.

If it is now a question, not of a suspension of particles of equal size, but of a mass of different radius values, we may imagine this mass of particles divided into a number of fractions, and, provided that $r_2 - r_1 = \Delta r$ is sufficiently small, we may take the amount of particles, $F(r)\Delta r$, in the interval r to $r + \Delta r$ to be of identical effective radii (Fig. 6). This limiting value for $\Delta r = o$ clearly becomes $F(r)dr$.

If ψ designate that portion of $F(r)dr$ which has fallen at a given point of time, then, up to a certain time, the above equation (2) holds good, and

$$\psi = \frac{F(r)dr \, . \, v}{h} t = \frac{F(r)drCr^2}{h} t \quad . \qquad (5)$$

The *whole* of this fraction has fallen down after a time t corresponding to the radius-value $\rho = \sqrt{\frac{h}{Ct}}$

We consider now a certain time t from the beginning of the deposition. There have then fallen on to the plate firstly all particles with a radius $<\rho$, that is

$$\int_\rho^\infty F(r)dr$$

secondly

$$\int_0^\rho \psi = \int_0^\rho \frac{Cr^2}{h} \, . \, t \, . \, F(r)dr.$$

But the sum of these weights is just the value of the function P at the time t

Therefore

$$P = \int_\rho^\infty F(r)dr + t \int_0^\rho \frac{Cr^2}{h} F(r)dr \, . \quad . \quad . \quad . \quad . \qquad (6)$$

But P as a function of the time is just the accumulation curve. By differentiating twice, solving for $F(r)$ and inserting the limiting values we get

$$F(\rho) = -\frac{2t^2}{\rho} \frac{d^2P}{dt^2} \quad . \quad . \quad . \quad . \quad . \qquad (7a)$$

$$t = \frac{h}{C\rho^2}; \quad \rho = \sqrt{\frac{h}{Ct}} \quad . \quad . \quad . \quad . \quad . \qquad (7b)$$

These equations enable us to calculate the values on the distribution curve for fixed values of ρ. The difficulty is to calculate the other differential coefficients of the accumulation curve with sufficient accuracy from the observed values of P. This is most conveniently done graphically, in the following manner:

If P_1, P_2, P_3, and so on, be the weights of the sediment at the times t_1, t_2, t_3, and so on, we may, provided that we have sufficiently small weights, write

$$\frac{dP}{dt} = \frac{P_2 - P_1}{t_2 - t_1}$$

and thus from the observation material *calculate* the first differential coefficient of the accumulation curve.

If we now set off as abscissæ

$$x = \log_{10} t = ln_e t \,.\, \log_{10} e,$$

and as ordinates

$$y = \log_{10} \frac{dP}{dt} = ln_e \frac{dP}{dt} \,.\, \log_{10} e,$$

we obtain a discontinuous curve consisting of horizontal parts. If we substitute for this a smooth continuous "auxiliary curve," we may determine the second differential coefficient of the accumulation curve from the angle-coefficient for the tangent of this curve. We here use logarithms with the purely practical object of avoiding excessively large and unwieldy figures.

$$\frac{dy}{dx} = \frac{\frac{d^2P}{dt^2}}{\frac{dP}{dt}} \cdot \frac{dt}{dx} \,.\, \log_{10} e = \frac{\frac{d^2P}{dt^2}}{\frac{dP}{dt}} \,.\, t \quad . \quad . \quad . \quad (8)$$

But equation (7*a*) may be written in the form

$$F(\rho) = -\frac{2t}{\rho} \cdot \frac{\frac{d^2P}{dt^2}}{\frac{dP}{dt}} \,.\, t \,.\, \frac{dP}{dt}$$

or, according to (8)

$$F(\rho) = -\frac{2t}{\rho} \cdot \frac{dy}{dx} \cdot \frac{dP}{dt} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

For the construction of the distribution curve we must in this equation decide upon fitting radius values ($\rho = 2\mu$, 1μ, and so forth), *calculate* the corresponding t-values according to 7*b*, *determine graphically* from the auxiliary curve $\frac{dy}{dx}$ for each value of t, and, finally, calculate $\frac{dP}{dt}$, either from the data of the observation or from the auxiliary curve, by finding the y-value corresponding to each value of log t.

Examples of calculations showing the method of working out have been previously published in the *Proc. Roy. Soc.*, Edinburgh,[1] and I only give in Figs. 8, 9, 9*b*, 10, 11, 16, 17, 18, and 19, some examples of the distribution curves obtained for various soils.

5. THE EXTENSION OF THE RESEARCHES TO SEDIMENTATION IN MORE VISCOUS LIQUIDS.

The use of sedimentation liquids of smaller specific gravity and viscosity, whereby the deposition would proceed more rapidly and an extension of the registered region to the left might be obtained in a reasonable time, cannot be carried out in practice. For with all liquids which could here come in question there occur, because the greater volatility, and the cooling of

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[1] Odén, *Proc. Roy. Soc.*, of Edinburgh, **36** (III.), No. 13, 219-35 (1916).

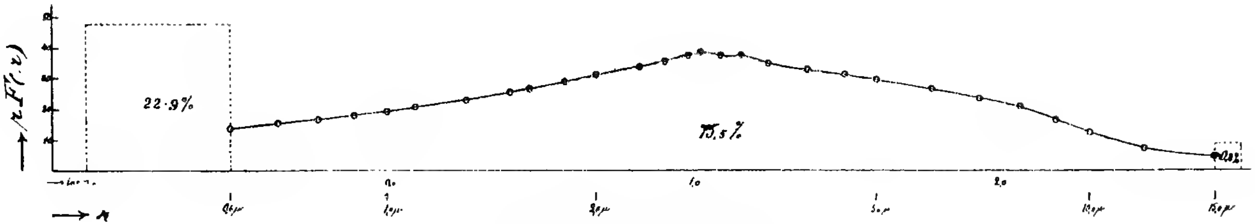

FIG. 8.—Ice-sea deposit, Frösön.

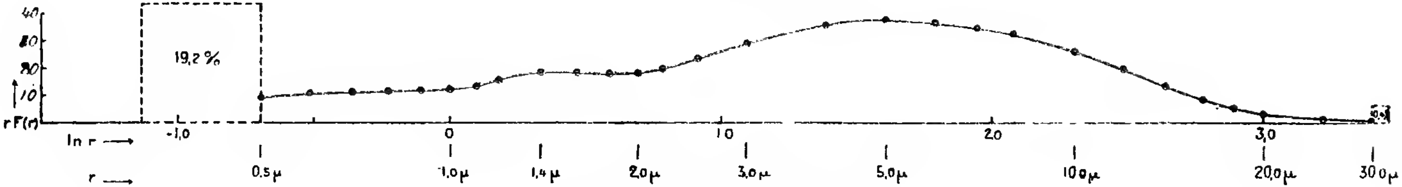

FIG. 9.—" Rhaet " clay, Bornholm.

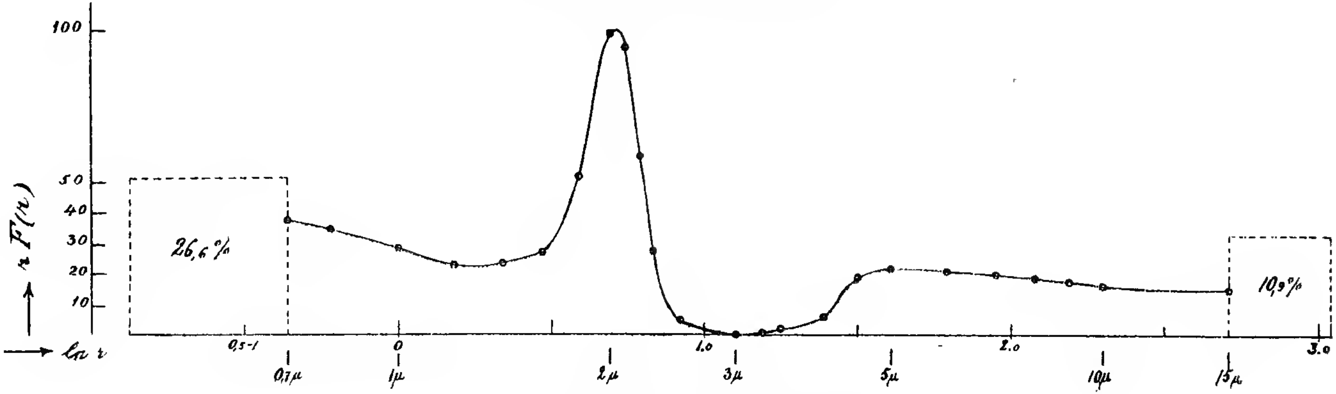

FIG. 9b.—Medium oligocaene silt from Skive.

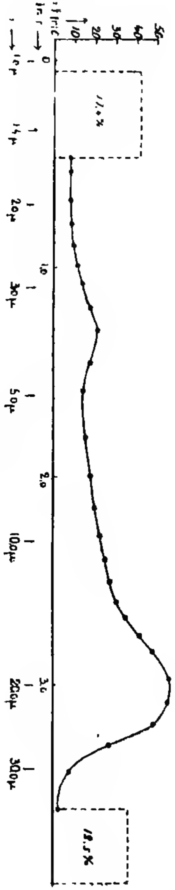

FIG. 10.

the surface caused thereby, convection currents which interfere with the deposition. On the other hand, an addition of glycerine (sp. gr. 1·3, viscosity about 11 at 15° C.) to the suspension under examination delays the deposition of sand and silt particles to such an extent that it becomes possible to observe particles up to $r = 50\mu$, that is, up to 0·1 mm. diameter.

An observation of this nature of a fairly coarse Danish mica-clay from the Upper Miocene strata at Vemb (near Lemvig) was carried out at 15° C. in a glycerine-water mixture of $d = 1·115$ and $\eta = 0·04925$, with a height of fall of 30 cm. I refrain from giving the observations and only give, in Fig. 10, the distribution curve calculated therefrom.

From 30μ the distribution curve may be regarded as fairly reliable. The coarser sand grains, which sink almost at once, are assembled together to the right.

As a proof of the correctness of the above assumptions and as an example of the method of working when it is a question of earths of particles very various in size, we may here give the figures from a research on a kaolin soil 107 Sandbäck.

Since it is impossible to observe the deposition of particles larger than 0·1 mm. in the sedimentation apparatus, the coarser material, "sand," was levigated out to begin with in the Atterberg levigation cylinder with a height of fall of 30 cm., and a time of fall of 15 seconds. After the dry weight had been determined, there had in this way been isolated $\frac{48·27}{100}$ as fraction A. According both to Oseen's[1] modification of Stokes' formula and to Atterberg's experimental results, this comprises the particles of an effective radius $> 100\mu$. It was not further examined, but was recorded as a square to the right in Fig. 11.

One further separation was carried out in the Atterberg cylinder at 15° C. and 20 cm. height of fall, for a period of 20 minutes. The particles no longer in suspension, "Fraction B," amounted to $\frac{19·87}{100}$, and the suspended portion, amounting to $\frac{31·86}{100}$, was taken as the residue, in good agreement with an analysis which showed 32 per cent. The two fractions, B and C, were then sedimented separately in different liquids, with different heights of fall, and at different temperatures.

	Specific D.	η.	Temperature.	Height of Fall.
Fraction B in water + glycerine .	1·125	0·05642	$15°_2$	15 cm.
Fraction C in water . . .	1	0·01155	$14°_5$	10 cm.

In spite of this the curves coincide in a quite unmistakable way, as is seen in Fig. 11, and give a picture of the mechanical constitution of the whole region from $0·4\mu$ to 100μ. The two small squares at 8μ indicate that the separation from the levigation was not quite complete, so that fraction B still contained some still finer particles. The levigations were carried out with a view to make possible the determination of the sand particles in a more viscous liquid. They were, certainly, separated in the Atterberg apparatus, but not according to the times of deposition fixed by him. Another matter, which, with regard to what follows, is worth noticing, is that my assistant, when calculating and drawing the curve, was given only the figures of the observation and the physical data, but otherwise received no further information regarding the origin of the sample, nor of any previous researches thereon.

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[1] C. W. Oseen, *Arkiv. f. matematik, etc.; Utg. av K. Svenska Vet. Akad. i., Stockholm*, **6**, No. 29 (1910); **9**, No. 16 (1913).

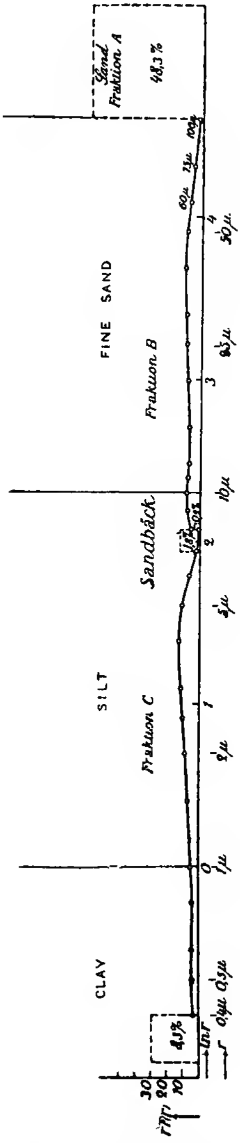

Fig. 11.

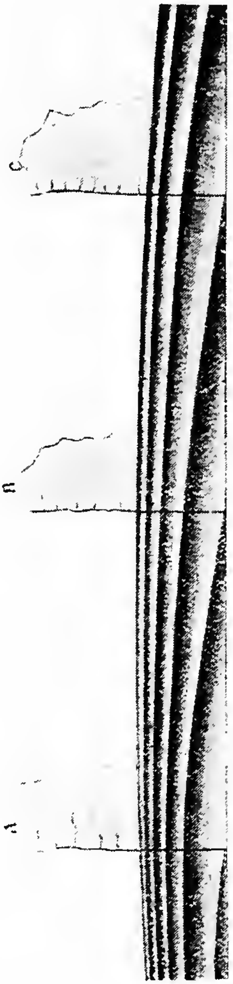

Fig. 12.—Diagrammatic section in the direction of the ice-edge through the lower strata of the stratified clay, according to De Geer. Three successive stages of the ice-edge, A, B, C, each with its corresponding layer of clay, *a*, *b*, *c*.

If we draw perpendiculars through the effective radii 1μ, 10μ, and 100μ, the distribution curve is divided into the International (Atterberg's) groups of clay, silt, fine sand, and sand. If the curve be drawn on millimetre paper the weights may easily be determined by counting the squares, thus giving the figures for a mechanical analysis of the soil.

These gave:—

Clay up to 1μ	(diameter 2μ) . .	13·0 per cent.
Silt 1·0μ to 10μ	(„ 2-20μ) . .	21·9 „
Fine sand 10μ to 100μ	(„ 20-200μ)	20·0 „
Sand > 100μ determined by levigation . .		48·3 „
		103·2 „

As we see, the calculations here gave a little more than 100 per cent., which is often the case, due to the uncertainty in the determination of the second differential coefficient of the accumulation curve.

It is of interest to see, not only that the curves plotted according to the new method show a good correspondence with each other, as shown above, but also how the figures for analyses which have been calculated from the distribution curves (obtained with the automatic registering apparatus) compare with others obtained by other means. Two different analyses of the same soil exist now, the one by A. Atterberg[1] and the other by Dr. C. Munthe[2] and I have further, as a check, determined the sand content with the Atterberg apparatus.

If we compare these figures we obtain the following:—

		Per Cent.	Mean Per Cent.
Clay (called both by A. and M. "residue")	Atterberg	14·0	12·85
	Munthe	11·7	
Silt	Atterberg	19·6	20·4
	Munthe	20·8	
Fine sand	Atterberg	21·1	21·9
	Munthe	22·7	
Sand	Atterberg	45·3	45·2
	Munthe	42·1	
	Odén	48·3	
			100·35

It has often been pointed out that the figures of the levigation analyses vary frequently according to the temperature and the operator. Despite this, the mean figures for the older analyses show a surprisingly good agreement with those given above, obtained by my method. It should be remembered that a part of the soil had been deposited in a glycerine mixture of a viscosity five times greater than that of water. The utility and correctness of the hydrodynamic equations is thus made obvious, and we may hope that they will in the future replace the empirical formulæ.

6. The Distribution Curves of some Annual Layers of the Swedish Stratified Clay.

As a second example we may here describe the use of the new method in the study of a geological problem.

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[1] Atterberg, *Intern. Mitt. f. Bodenkunde*, **2**, 26 (1912).

[2] *Dissertation*, Upsala, 1915, p. 37.

We have in the Fennoscandian quaternary deposits a remarkably widely-distributed clay showing a clearly marked stratification, which has from olden times been called "the stratified clay".

Formerly, opinions regarding the cause of this stratification diverged widely, until Gerard de Geer, in the early eighties (1882) connected the stratification with the melting of the great northern inland ice, and characterised the different layers as annual deposits from the melted ice from the glaciers of the retreating ice-line. The later development of this theory has, as is well-known, led up to the geochronological researches on the recession of the ice, and made it possible to estimate exactly geological time over a period of more than 12,000 years.[1]

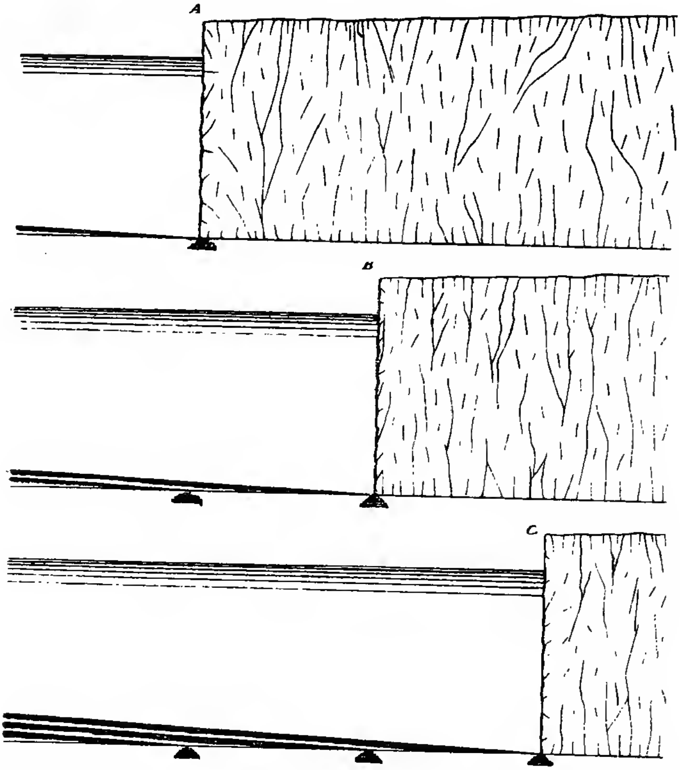

FIG. 13.—Schematic view according to De Geer, showing three successive stages of the ice-edge. The black triangles represent the coarse, stony "ås".

This is not the place to give even the outlines of de Geer's magnificent researches. Only as much as is necessary to understand the following mechanical analyses will be reviewed, with the help of two of de Geer's diagramatic figures (see Figs. 12 and 13). At the time of the melting of the great inland ice, Fennoscandia was covered by an Arctic sea, though poor in salt content, into which large masses of sand, morain, and clay, formed by glacier-erosion, were carried by the glacier streams.

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[1] G. de Geer, *Geochronologie der letzten* 12,000 *Jahre Geol. Rundsch*, 1912, p. 457.

As far as we can judge, these streams must have flowed in tunnels under the inland ice. The larger stones and blocks were deposited at the gates of the glaziers or near the edge of the ice, and remain still as the mounds (ås) characteristic for Sweden.

The nearer the ice edge the deposition occurred, the larger and more quickly falling were the particles deposited: while the particles which, on account of the low salt-content of the water, were held in suspension for a long time, were deposited further out over a large surface. As the heaviest gradually subsided, the clay became finer and finer, the farther it was from the ice edge. Since the melting was strongest during the summer, and produced streams of melted ice more rapid, and of greater carrying-power, the structure of the annual deposits shows that the lower part is built up of coarser and lighter-coloured particles of brown to grey clay, which finally merges into a thin, dark, nearly black, so-called winter layer.

During the summer the ice-edge retreated a little (according to de Geer, 50 to 350 metres) northwards, while, during the winter it stood still, or even advanced a little. Due to this movement of the ice-edge each newly formed layer of clay came to rest with the edge nearest the ice on sand, while, further back, it covered the layer of the year before.

The stratified clays resemble in structure fish scales in the respect that each new deposit on the side towards the ice-edge projects a little over the one beneath, the overlap giving the distance that the ice had retreated during the year, and the breadth of ground laid free. This is shown diagrammatically in de Geer's Figs. 12 and 13. A vertical section of the clay, therefore (*cf.* Figs. 14 and 15), shows layers that become thinner and thinner the higher in the section they lie, corresponding to the northward movement of the ice-edge.

De Geer's explanation of the stratification obtained strong corroboration through A. G. Högbom's[1] chemical researches on a calcareous stratified clay. It was shown that the light (grey) "summer deposits" were appreciably richer in lime than the dark (black) winter layers.

The cause of this must be sought in the quicker and more complete solution of the lime during the long time of suspension of the particles, and also in the greater solubility resulting from the larger surface-area due to the greater degree of fineness. Extraction of carbonate of lime during water suspension was also experimentally demonstrated by Högbom.

But the mechanical constitution, too, of the layers, as shown by the distribution curves, must reveal their history. As little work of this nature has been done on the quaternary clays, I have investigated some of these clay-strata.

The thickness of the strata varies a great deal. The lower strata may show a thickness of several decimetres, but this diminishes as we go higher until the thickness is not more than a millimetre, or even a fraction thereof. Higher up the streakiness disappears, and the clay takes a homogeneous grey-brown tone, with here and there a striated appearance. This brown-grey clay merges higher up into the postglacial overlying clay strata, deposited in the Ancylus Lake and the Litorine Sea. Between these two occurs in some places the so-called mottled zone with small lime concretions.

The samples investigated by me were taken from a clay quarry at the St. Erik brickworks, about a kilometre North-West of Upsala. (The appearance is shown in Fig. 14). Reckoning from the bottom up, the following layers were investigated:—

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[1] *Trans. of the Geological Soc.*, Stockholm, 11, 265 (1889); 14, 291 (1892).

A. A 5 cm. summer deposit.
B. " 4 " " "
C. " 2 " " "
D. An area where the striæ were to be measured in mm. (Summer and winter layers.)
E. An area where the striation could scarcely be distinguished, but where the clay certainly did not belong to the "stained zone".
F. The over-lying, very thick, Ancylus clay, taken just over the mottled zone. (Fig. 17.)

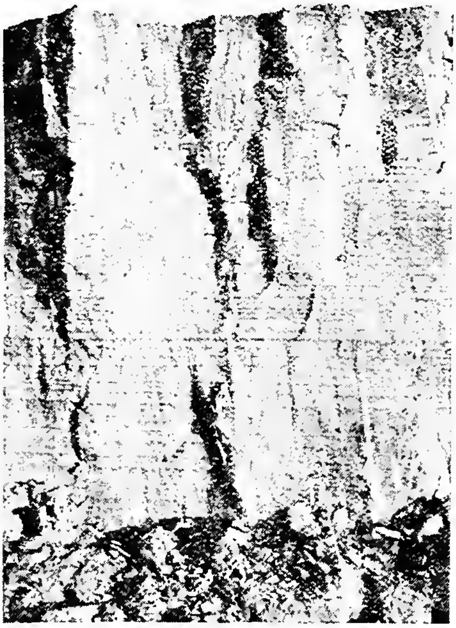

FIG. 14.

The preparatory treatment of all the samples was carried out according to the standard method published by me.[1] A detailed report of the figures of the original determinations would take too much space, I content myself, therefore, with giving graphically in Figs. 16 to 20. the course of the distribution curves.

In setting out the results in Fig 16, the smallest particles ($<0{\cdot}6\mu$) are shown to the left as a square, proportional to the weight. The coarser particles showing, in places, to the right clearly do not belong to the true clay deposit, but are to be regarded as sandy impurities, dropped by drifting icebergs.

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[1] *Bull. Geol. Institut. of Upsala*, **16**, 125 (1919); *Intern. Mitt. f. Bodenkunde*, **10**, 320 (1920).

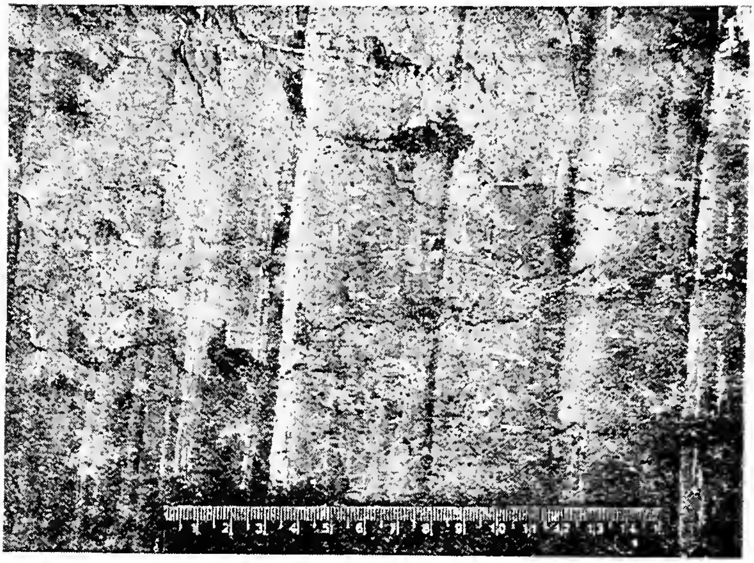

Fig. 15.

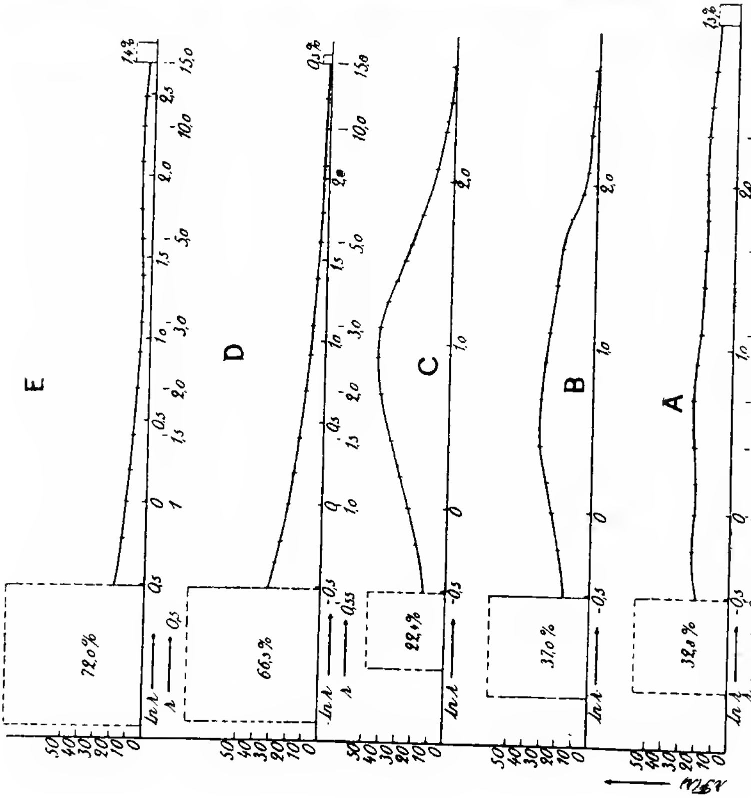

Fig. 16.

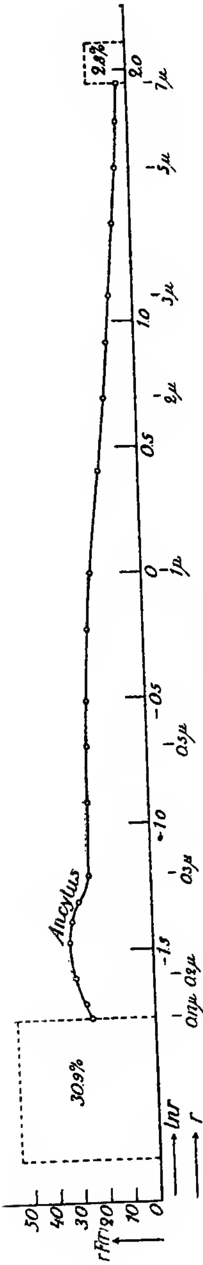
2.8%
2.0
7μ
5μ
3μ
1.0
2μ
0.5
0
1μ
−0.5
0.5μ
−1.0
0.3μ
−1.5
0.2μ
0.11μ
Ancylus
30.9%
ln r
r
0
10
20
30
40
50
rF(r)

FIG. 17.

If we disregard these irregularities, the samples in Fig. 16 show the increase in coarser particles with increase of thickness of the layer, just as the de Geer theory requires.

The experiment with the Ancylus clay was allowed to proceed for a much longer time, and the curve was continued a long way to the left, as far as an effective radius of 0·17, as shown in Fig. 17.

After this, the mean diameter of the still undeposited residue was determined by the Zsigmondy-Siedentopf method (*cf.* p. 329). The figures are not completely comparable, since the temperature was not quite the same during all the determinations; and further, there is always a fairly large error in such determinations. But if we examine in turn E, D, C, and A, we find a regular increase in the mean size of the grains. It is also of importance to note that the thicker layers likewise contain appreciable quantities of quite fine particles, which have clearly been deposited together with the coarser grains.

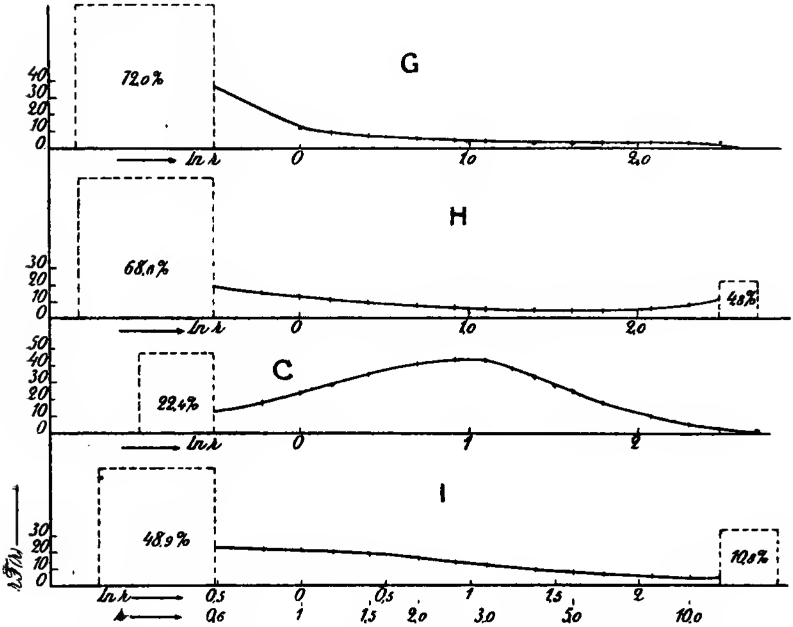

FIG. 18.

Comparative investigations of "winter" and "summer" deposits were then carried out.

G. A millimetre thick black winter deposit overlying a 1 cm. thick summer deposit.

H. } The winter deposits both overlying and underlying the 2 cm.
I. } summer deposit C.

The distribution curves for these clays are given in Fig. 18, and clearly show the finer structure of the winter deposit. The appearance of G shows good agreement with the sample E, from the finest deposits, which was to be expected, since the latter consists of both winter and summer deposit.

Further corroboration is furnished by the distribution curves for the samples in Fig. 19.

K. A winter deposit overlying a 4 cm. thick summer deposit.
L. } The winter deposits both overlying and underlying the 5 cm.
M. } thick summer deposit B.

If the winter deposits be compared with each other, they too show a regular decrease in the amount of fine material with increasing depth. The sample, H, certainly is an exception, but this contains considerable quantities (10 per cent.) of coarse sand as impurity.

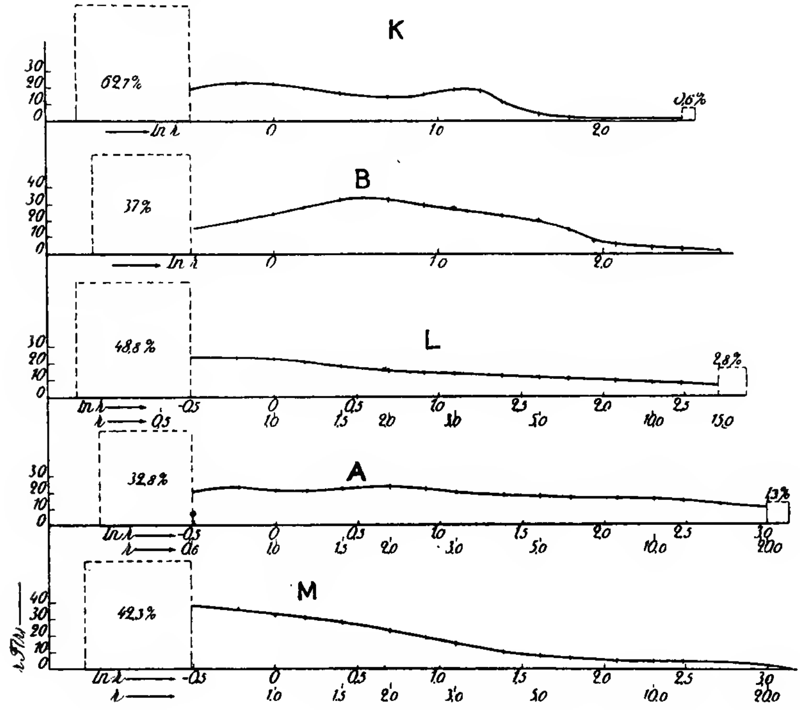

FIG. 19.

With increasing thickness of the layers, the differences between the summer and winter deposits become less marked, as is shown by a comparison of Figs. 18 and 19. This is appreciable, indeed, to the naked eye, since the colour difference between the black winter deposits and the more grey-brown summer deposits give place to a more monotonous grey-brown.

The colour, therefore, is dependent on the size of the particles, and perhaps also on changing chemical constitution dependent thereon.

THE MECHANISM OF FLOCCULATION IN SOILS.

By Norman M. Comber, B.Sc., A.R.C.S., A.I.C. (Department of Agriculture, The University, Leeds).

The texture of a mineral soil is determined by two chief factors, namely the size of the particles and the arrangement of the particles.

The size of the ultimate particles is manifestly permanent and unalterable for all practical purposes. Information regarding this factor is of great importance, and for the purpose of obtaining and expressing such information the soil particles are conventionally graded. In this country it is customary to divide all particles capable of passing a 3 mm. sieve into six "fractions," namely,

1. Gravel	3 – 1 mm. diam.
2. Coarse Sand	1 – ·2 mm. diam.
3. Fine Sand	·2 – ·04 mm. diam.
4. Coarse Silt	·04 – ·01 mm. diam.
5. Fine Silt	·01 – ·002 mm. diam.
6. Clay	below ·002 mm. diam.

The finer fractions are separated by sedimentation; the coarser ones by sieving.

The arrangement of the particles in a soil is by no means permanent, but is liable to relatively rapid changes. Besides the obvious rearrangement which will be caused by compressing or by loosening the soil, the smallest particles (the fine silt and the clay) become under certain conditions aggregated together to produce what is, in practical effect, a lesser number of larger particles and a consequent lightening of the soil. This aggregation or flocculation process is affected by a number of conditions such as freezing and thawing, sun-drying, and the presence of electrolytes. It is reversible, and deflocculation follows the removal of the factor causing flocculation.

In this paper it is proposed to offer some observations regarding this flocculation process as it is brought about by electrolytes in general, and by lime in particular.

The Effect of Fertilisers on Soil Texture.

It is well established by experience and experiment in the field, that the addition of certain fertilisers has an effect upon the soil texture. Thus, the excessive or prolonged use of nitrate of soda (which has been shown by Hall[1] and his co-workers to give rise to sodium carbonate in the soil) is known to enhance the stickiness of a soil, and to so deflocculate the clay that it is removed in measurable amount in a turbid drainage water. Laboratory experience abundantly confirms the field observation that small amounts of alkaline substances, such as the carbonates and hydroxides of sodium potassium and ammonium, deflocculate soil clay giving it the power of remaining in suspension almost indefinitely, making it very difficult to filter and rendering it extremely sticky when in mass.

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[1] See "The Book of the Rothamsted Experiments" (1919), pp. 295-305.

By far the most striking and the most important case which arises in agricultural practice is the amelioration of the texture of clay soils which results from the addition of lime. It is established by the experience of many generations that dressings of lime of the order of one to two tons to the acre greatly diminish the stickiness of a clay soil, reduce the plough draught and facilitate drainage. The laboratory examination of the subject shows that this action of lime is due to the aggregation or flocculation of the particles.

In farming practice, however, it is not an invariable rule that lime thus improves the texture of all heavy soils. Field experience shows that there is a distinction between heavy soils which respond, in respect of their texture, to dressings of lime and those which do not so respond; and this distinction is found to coincide with that between heavy soils containing a dominant amount of the clay fraction and those whose heaviness is due to a dominant amount of the fine silt fraction. *Clay is readily flocculated by lime, fine silt is not.*

THE FLOCCULATION OF SOILS AND THE ISOELECTRIC POINT THEORY.

There have been very many investigations of the power of various electrolytes and colloids to flocculate suspensions of soil particles and of kaolin. In general the results indicate a process analogous to the flocculation of suspensoid sols, and which admits of explanation on the basis of the isoelectric point theory.

For instance, if a series of similar suspensions of soil particles is treated with colloidal ferric hydroxide in amounts which gradually increase from one end of the series to the other, a point of optimum and immediate flocculation can be found, and amounts of the positive sol greater or less than that producing the optimum flocculation, have less effect. Similar results can be obtained by the use of ferric chloride, aluminium hydroxide, and aluminium chloride.[1] Such results are analogous to those obtained by Burton [2] in the flocculation of metal sols by aluminium salts.

Again, with electrolytes as flocculants the valency rule is applicable as well to the flocculation of soil suspensions as to that of suspensoid sols. Hall and Morison [3] in a careful investigation of the flocculation of kaolin suspensions certainly failed to elicit the quantitative requirements of Whetham's theory, but they showed quite clearly that the trivalent kations of salts had a flocculating power superior to that of divalent kations which in turn were more effective than monovalent kations.

The flocculation of soil particles appears therefore to fall fairly well into line with the flocculation of suspensoid sols and, with the flocculation of these sols, to be amenable to the isoelectric point theory. There is, however, one well-known exception which happens to be the only case of soil flocculation which is of great practical importance. The flocculation of clay by lime does not appear to be compatible with the electrical theory, since the hydroxyl ion will, according to the theory, tend to stabilise the suspension.

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[1] Comber, *J. Agric. Sci.*, 11 (1921).

[2] See Burton, "The Physical Properties of Colloidal Solution" (1916).

[3] Hall and Morison, *J. Agric. Sci.*, 2 (1907), 244.

THE FLOCCULATION OF CLAY BY LIME.

The explanation of this anomalous case of flocculation which is commonly advanced is that lime added to the soil becomes converted into calcium bicarbonate which latter compound then acts as the flocculant. This explanation is, however, difficult to accept for several reasons of which the following are the chief:—

(i) It affords no explanation of the difference between the action of lime on clay and on fine silt.

(ii) If two similar clay suspensions are treated, one with calcium hydroxide and one with calcium bicarbonate in equivalent amount, flocculation is much more rapid in the former case. (The reverse is true of suspensions of fine silt and, as shown by Hall and Morison, of kaolin.)

The present writer has examined the effect of alkalinity on the flocculation, by calcium salts, of clay and of fine silt suspensions.[1] It was found that *the flocculation of clay by calcium nitrate is greatly enhanced by the addition of a small amount of ammonium hydroxide, while the flocculation of fine silt by calcium salts is retarded by the addition of alkali.* It must also be noted that the volume of the coagulum is noticeably large when compared with the volume of the coagulum formed by neutral salts.

It seems clear, then, that the flocculation of clay by lime is a genuinely abnormal case in which the hydroxyl ion actually facilitates the action.

THE MECHANISM OF FLOCCULATION IN SOILS.

In endeavouring to find an explanation of clay flocculation in general and of the abnormal effect of alkalinity upon the flocculation of clay by the calcium ion in particular, it is necessary to bear in mind two important and pertinent facts about clay, namely.

(i) Clay is very reactive. With solutions of neutral salts it enters into the process of base exchange, and for this reason the flocculating effect of salts is not to be interpreted as necessarily and entirely a direct effect of the kation of the particular salt used. Also, clay is readily susceptible to dissolution by acids, and flocculation by acids will be complicated accordingly.

(ii) The clay particle in water does not present a sharp solid-liquid surface. The relationship of clay to water is different from that of other soil fractions, kaolin and ignited clay,[2] and the peculiarities of clay in this respect strongly indicate that the clay particle is related to the water through the intermediation of organic and siliceous colloidal matter. Unignited soil clay seems to stand apart from other fractions and from kaolin by reason of its marked protection by "emulsoid" material.

Taking cognisance of these two facts about clay—its reactivity and its protection[3]—it seems clear that three cases of flocculating action may be possible, namely:—

1. *Direct flocculation* in which the flocculant acts in the same manner as on unprotected and non-reactive suspended particles, the action being merely diminished or delayed by reason of the protection.

There are probably few, if any, cases in which the flocculation of clay is exclusively of this type. The action of iron and aluminium salts and of the colloidal hydroxides of iron and aluminium may be predominantly a direct action. A concentration of these flocculants which produces a maximum effect is easily observable and in this respect the phenomenon seems to be analogous to the flocculation of metal sols.

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[1] Comber, *J. Agric. Sci.*, 10 (1920), 425.

[2] See Keen, *ibid.*, 44.

[3] Regarding protection of clay by humus, see Sven Oden, *J. für Landwirt* (1919), p. 177.

2. *Indirect flocculation* in which the products of a previous reaction, such as base exchange or dissolution, act as flocculants.

When neutral salts are used as flocculants it seems assured that the action is to some extent of this second type. There is invariably a partial exchange of kations when neutral salt solutions are in contact with clay, the base exchange process is very rapid and it appears inevitable therefore that some part of the flocculating action is due to the kations brought into solution from the clay.

The flocculation of clay by acids seems also to be largely indirect and attributable to the action of aluminium, etc., dissolved by the acid from the clay. In the flocculation of kaolin Hall and Morison[1] found that mineral acids were slightly better flocculants than aluminium salts, and suggest that the flocculating power of the latter may be partly due to the acid formed by hydrolysis. With soil clay the case seems to be the reverse of this. Using hydrochloric acid and aluminium chloride in one set of experiments, and sulphuric acid and aluminium sulphate in another, and using several different clays, the present writer has found that the aluminium salts flocculate soil clay much more rapidly than the corresponding acid in equivalent amount.[2] It is therefore suggested that the action of acids may to some extent be ascribed to the bases they bring into solution.

3. *Abnormal flocculation* in which the flocculant reacts with the protecting emulsoid matter forming a coagulum which entrains the particles.

This type of clay flocculation seems to be of greatest agricultural importance for it appears to provide a feasible explanation of the abnormal flocculation of clay by lime, the fact of which has been described above.

When calcium hydroxide is added to a dilute silicic acid sol, a gelatinous precipitate is formed. This precipitate is not formed when a *neutral* calcium salt is added to the neutral sol: it is produced by the action of calcium ions only when the medium of action is alkaline. The precipitate has been investigated by Le Chatelier[3] who found that it consisted of silica with varying amounts of lime, and that the lime is easily and entirely removed by washing. Another feature of this precipitate is its enormous volume: according to Le Chatelier 1 gram of it settles to occupy a volume of 2 litres.

Now if the protection of clay particles is in part due to colloidal silica, which seems certain to be the case, then the addition of lime—the addition of calcium ions and hydroxyl ions—will produce a precipitate such as that described. The production of such a precipitate, entraining the particles, seems to be a satisfactory explanation of the flocculation of clay by lime. It accounts for the fact that alkalinity facilitates the flocculation since the formation of the precipitate is dependent upon alkalinity. It accounts for the reversibility of the action since the precipitate is hydrolysed by washing. It accounts for the large volume of the clay coagulum since the precipitate is phenomenally voluminous. Further, this theory of the abnormal flocculation of clay by lime, postulates nothing about clay other than a siliceous emulsoid protection which is already strongly indicated by quite independent considerations.

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[1] *Loc. cit.*

[2] Comber, *J. Agric. Sci.*, **11** (1921).

[3] "La Silice et les Silicates" (1914).

The effect of small amounts of colloidal silica on the flocculation of finely divided particles in suspension was examined by using a sample of oxide of iron in the form of an impalpable powder. The oxide of iron, when shaken with pure water did not remain long in suspension, but traces of silicic acid sol gave not only stability to the suspension but also the power of being flocculated by calcium salts much more readily in the presence of alkali than in neutral suspension. It was found in one case that 0·6 mgms. SiO_2 was able to affect 300·0 mgms. of the oxide of iron in this respect. Evidently, therefore, very small amounts of colloidal silica in conjunction with finely divided particles can produce a system susceptible to the abnormal flocculation which is found in the case of clay.

While, then, the mechanism of flocculation in soils does not generally appear to be essentially different from that of the flocculation of suspensoid sols, the flocculation of clay by lime is a process of a distinctly different type. Using the prevalent terminology it is an "emulsoid" phenomenon and is quite out of line with the flocculation of "suspensoids". As an emulsoid phenomenon it appears to be explicable on the basis of the reaction between calcium hydroxide and colloidal silicic acid, and the assumption, which that explanation involves, of a particular colloidal condition which differentiates clay from other soil fractions and from kaolin, is consistent with the peculiarities of clay which have been brought to light by other investigations.

ON THE PLASTICITY OF CLAYS.

By J. W. Mellor, D.Sc.

1. Definition of Plasticity.

The fictile qualities of a clay are primarily dependent on its plasticity. Plasticity is the property which enables a clay to change its shape without cracking when it is subjected to a deforming stress. The elasticity of the wet clay is negligibly small. Clay is peculiar in possessing another quality which is as important as plasticity. It has a high binding power when dried and fired, so that the form impressed on the plastic clay is retained more or less persistently when the clay is dried and fired. Very fine powders —barium sulphate, glass, quartz, etc.—acquire a kind of plasticity when wetted, but when dried, the binding power is exceedingly small. They are plastic but their plasticity cannot be used in the fictile arts because the second quality is wanting.

Many definitions of plasticity confuse these two distinct properties and assume that the binding power of the dried clay is implied in the term plasticity. Indeed, many methods proposed for measuring plasticity are based on the binding power of the dried clay. It is assumed that the tenacity of the dried clay is proportional to the plasticity of the wet clay. This is generally but not always true. No known property of the dried clay can be used as an infallible index of the plasticity of the wet clay, and measurements of plasticity dependent on some property of the dried clay can therefore be dismissed, because even though they may measure an important property of clay, that property is not plasticity.

2. Mechanical Analysis of Plasticity.

It is really difficult to measure the plasticity of clay because the property is somewhat complex. A. Brongniart (1844) recognised its elusive character. He said: *On a souvent parlé de cette propriété, on semble la connaître, mais on n'en a qu'une vague idée.* The potter's thumb is one of the most sensitive tests at present known, but that is not always satisfactory. B. Zschokke (1903) analysed plasticity into (i) the deformability; (ii) the cohesion; (iii) the adhesion; and (iv) the viscosity or internal friction of the clay. A. Martens (1898) represented plasticity, P, as being proportional to the toughness, T, of the material, and inversely as the modulus of rupture, R, such that $P = T/R$; H. Fischer (1884) added that the plasticity also varies inversely as the elasticity, e, of the material so that $P = T/eR$. These ideas resolve themselves into the assumption that

$$\text{Plasticity} = \frac{\text{Cohesion}}{\text{Internal friction}},$$

so that in estimating the plasticity of a clay, the potter's thumb is perhaps unconsciously affected by at least two effects—possibly more. There is first the internal friction which can be otherwise represented as the resistance which the clay offers to changing its shape; and second, there is the cohesion, *i.e.* the amount of deformation which the clay can suffer without cracking. F. F. Grout (1905) worked on these lines.

Plasticity is taken to vary proportionally with each of these factors, so that if P denotes the plasticity of the wet clay; r, the resistance the clay offers to changing its shape; and s, the amount of deformation which the clay can suffer without cracking, then, with a and b constants,

$$P = k(r + a)(s + b)$$

where k is the constant of proportion. Each of the factors r and s can be measured and from these results P can be calculated. By a suitable choice of units, or by conventionally regarding the apparatus used in a measurement as the standard for comparison, the constant k cuts out and we can write $P = (r + a)(s + b)$.

There is a quality in plasticity. The deformation pressure of some clays is greater than others, and such clays are said to be "stiff" or "strong". Some strong clays offer a high resistance to changing their shape and yet cannot be deformed very much without cracking. In other words, the clay is "strong" and "short". Many London clays might be cited in illustration. There are other clays which have a low deformation pressure, and can suffer little deformation without rupture. Some of the siliceous pipe-clays illustrate this type of clay. They are "weak" and "short". Other "fatty" clays offer a low resistance to change of shape, and yet suffer a comparatively large deformation without rupture. The black ball clays show this quality.

3. The Measurement of Plasticity.

The plasticity of a clay varies with the proportion of water in a curious way. As water is progressively added to a dry clay, the plasticity continually increases and attains a maximum value. Any further addition of water reduces the plasticity; the clay assumes another form. The particles no longer have a marked tendency to cohere together, rather does the clay become "sticky," and it adheres to anything it touches which water can "wet". In the sticky stage the clay is no longer workable. As more and more water is added, the clay assumes the form of slip, and can then be poured like a liquid.

It is therefore interesting to measure the relations between the proportion of water in the clay and the resistance the clay offers to changing its shape, and the deformation the clay can suffer without cracking. The results give two curves, $r = f(w)$, and $s = f'(w)$, and when the data are substituted in the equation $P = f(w) \cdot f'(w)$, they give a curve, Fig. 1, which simulates the observed phenomena by showing that the plasticity increases up to a maximum with increasing proportions of water. It is difficult to get concordant measurements, and the following method of measurement is not satisfactory, but it represents the present stage of the work of Messrs. G. E. Stringer and W. Emery which will be published later.

A sphere of the clay mixture is made 2 cm. in diameter. This is difficult. Messrs. G. E. Stringer and W. Emery gave a lot of attention to this subject in 1913, and their final mould was arranged as in Fig. 2. It represents an ordinary metal mould fitted with small spring cylinders *ss*, which release the sphere from the mould in which it has been pressed.

Cylindrical test pieces were not so satisfactory as the spherical ones. The sphere was placed about the centre of a weighed glass-slab and weighed. The glass-plate and sphere were then placed at A in the machine illustrated in Fig. 3. The disc A is adjusted until it just touches the sphere, and its position noted on the index I. Sufficient fine shot is run into the bucket B, to make the piston descend. The descent of the piston is stopped when vertical cracks appear on the edges of the clay disc. The mirror M allows the back of the disc to be readily seen. The distance moved by the descending piston is taken to represent the amount of deformation the clay could suffer without cracking; and the weight of the bucket of shot required to compress the clay spheres a definite distance is taken to represent the resistance the clay offered to changing its shape. The glass slab and clay disc are dried at 110° and the loss in weight allowed the percentage of moisture in the original clay to be calculated.

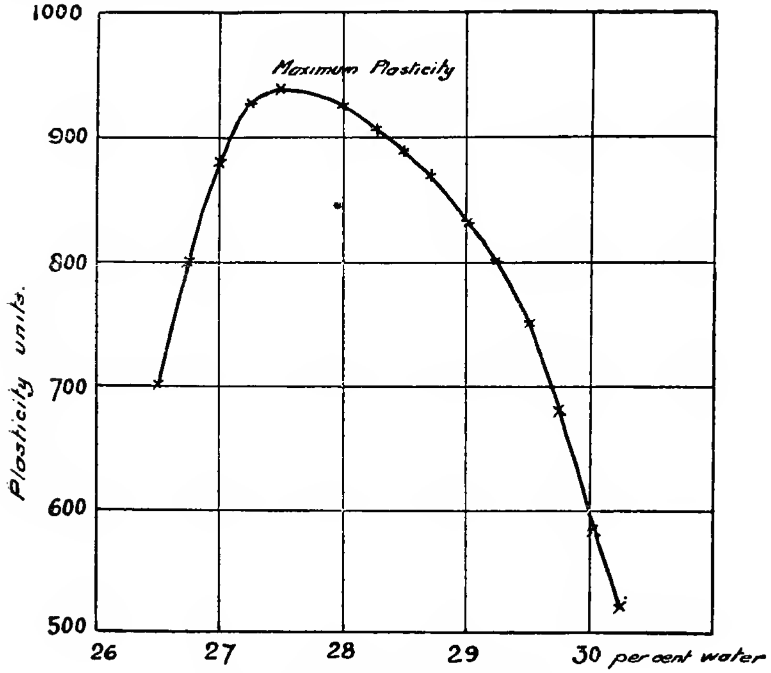

FIG. 1.—Plasticity curve of Ball Clay.

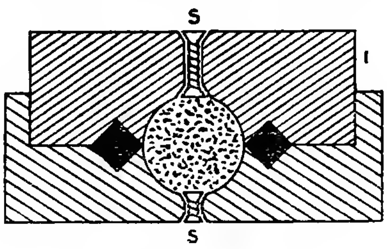

FIG. 2.

4. The Effect of Pressure on the Maximum Plasticity.

The state of maximum plasticity represents the best working condition for the clay, but that is so near the state of stickiness that, to allow a safe working margin, the clay should be worked with a little less water. Another point, the greater the moulding pressure applied to the clay, the smaller the proportion of water required to develop maximum plasticity, and the smaller the proportion of water required to make the clay sticky.

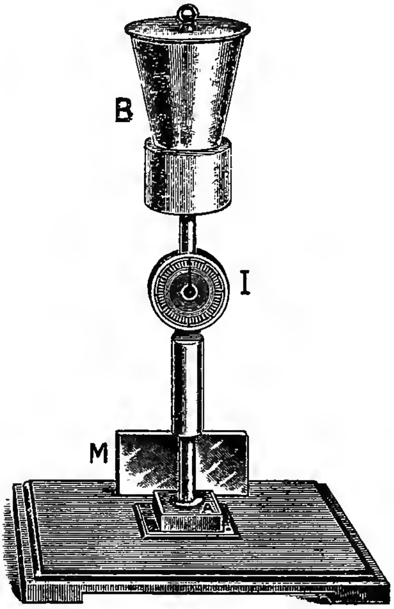

Fig. 3.

TABLE I.

Maximum Plasticity of Wet Clay Developed at Different Pressures.

Pressure, Kgrms. per Sq. Cm.	Water, Per Cent.
200	5·6
150	8·8
100	12·5
50	19·2
25	23·0
1	26·4

This point is easily tested by subjecting wet clay to different pressures and observing the pressure at which the clay sticks to the tool. With an earthenware body mixture the sticky stage developed at the pressures shown in Table I. when the clay contained the proportions of water indicated. This is rather an important consideration in preparing clays to be worked by machine processes.

5. The Physical Analysis of Plasticity.

Plasticity is a mechanical property, the resultant effect of a deformation and a pressure. The deformability of a clay is probably determined by the distances the particles can move without loss of cohesion; and the deformation pressure represents the magnitude of the cohesive or attractive forces as shown by the resistance offered by cohesion to the movements of the particles under the influence of an impressed force. The deformability of the clay is then conditioned by the size and shapes of the particles; and the deformation pressure is determined by the magnitude of the cohesion between the clay particles and the water, and by the thickness of the water film.

Until it has been shown that plasticity is a definite function of some other quality—dye-absorbing property, viscosity of slip, etc.—it cannot be assumed without reservations that measurements of these qualities measure plasticity. The claims made on behalf of such indexes of plasticity are arguments in a circle. Take the dye-absorbing test which I used in 1905. Plasticity is assumed to vary with the amount of colloid in a clay; the amount of colloid in the clay is then assumed to be proportional to the amount of dye the clay can absorb from a standard solution. Hence, dye-absorption measures plasticity. Obviously, a lot of work has to be done before this can be accepted. The viscosity test is in exactly the same condition.

Some methods which have been proposed for measuring plasticity really measure only one of the two components—deformation and pressure—into which plasticity has been resolved. For example, the so-called Vicat's needle test, A. Brongniart's wad-box test (1844), P. Jochum's bending test (1899), and K. Dummler's spiral test (1908), ultimately measure deformation, not pressure; and they give comparable results under constant conditions for a particular type of clay when the pressure is constant, but not necessarily so for different types of clay.

6. Plasticity and Colloidal Clay.

The plasticity of a clay is often assumed to be inversely proportional to the grain-size. H. E. Ashley (1909), for example, made this an essential part of his formula. The observation has been qualitatively recognised for a couple of centuries. A. Baumé in his *Mémoire sur les argilles ou recherches et expériences chymiques et physiques sur la nature des terres les plus propres à l'agriculture* (Paris, 1770) attributed the high plasticity of clays to their extremely fine state of subdivision, and to their containing some saline matter. He said:

> On doit attribuer le liant des argilles à l'extrême division de leurs parties qui les rend propres à retenir l'eau, et à leur état salin qui leur donne la faculté d'être presque dissolubles dans l'eau. Leurs molécules sont beaucoup plus dans l'état de division, que celui qu'on pourroit procurer à une pierre quelconque par des moyens méchaniques. On peut bien donner au sable et à toutes les matieres vitrifiables beaucoup de liant en les réduisant en poudre impalpable sur le porphyre; mais quelque divisées que soient ces substances, elles ne peuvent jamais acquérir le liant des argilles, parcequ'elles n'ont rien de salin qui les rende miscibles à l'eau; les argilles elles-mêmes n'ont presque plus de liant lorsqu'on leur a enlevé leur acide, quoique la substance terreuse reste dans le plus grand état de division.

If A. Baumé's *état salin* be translated "matter in a colloidal state," then his paragraph might have been written to-day. The meaning is clear; superposed on the plasticity exhibited by fine-grained powders, clays have a plasticity in virtue of their contained saline or colloidal matter. A Baumé thus approximates to the assumption made by T. Way in 1850, T. Schlösing in 1870, P. Rohland in 1902, and by H. E. Ashley in 1909, that plasticity is proportional to the amount of colloidal matter in the clay—*l'argile colloïdale* of T. Schlösing—and inversely as the state of subdivision. If, as appears highly probably, the plasticity of clay is proportional to the amount of colloidal matter in the clay, the dye-absorption test is probably invalid because there is nothing to show that the colloidal matters in different clays have the same absorption power. It is fairly certain that the colloidal matter in different clays is not the same, for this must be largely determined by the nature of the organic matters associated with the clay at the time of its deposition, or which have been afterwards acquired from extraneous sources.

Clays have qualities which might be predicted from the known properties of matter in the colloidal state. It is therefore assumed that clays contain x per cent. of colloidal matter possessing qualities like those possessed by the clay itself. This explanation recalls A. Baumé's *saline matter*, and the *terra pingua* of the mediæval chemists. The plasticity of clay has been attributed to both these imaginary substances. Indeed, just as in mediæval times every chemical process which was not understood was explained by an assumed *terra pingua*, or phlogiston, so now, we are inclined to attribute to the colloids every quality of clay which is not understood. Nevertheless, I believe a modified colloidal hypothesis gives the best working explanation of several properties of clay, even though it must be added that we have not progressed very far in advance of the eighteenth century. Calling the same thing different names is not getting along very fast.

7. PLASTICITY AND THE GRAIN-SIZE OF CLAYS.

The evidence for the statement that plasticity is inversely proportional to grain-size is not to be accepted without reservations. B. Zschokke (1903), and F. F. Grout (1905) have both shown that the plasticity of some clays is not influenced by finer grinding, and that the plasticity of other clays is lessened by fine grinding. This shows that close packing is also concerned in the action. It follows that closer packing is possible with mixed fine and coarse grains than with all fine or all coarse grains, and U. Aleksiejeff and P. A. Cremiatschensky (1896) have shown that both extremely fine-grained and extremely coarse-grained clays are less plastic than clays containing mixed fine and coarse grains. Hence, if grinding makes the particles more uniform in size, the clay will become less plastic; and it is probable that, other things being equal, the distribution of grain-sizes which permits the closest packing of the particles, will be most favourable to high plasticity.

8. THE EFFECT OF ACIDS, ALKALIES, AND SALTS ON THE SEDIMENTATION OF CLAY.

Plasticity *per se* can be readily explained by the known properties of films of water, and theories have been devised which postulate special shapes for the predominant particles in the clay, *e.g.* H. le Chatelier (1910) postulated flattened particles; and W. Olschewsky (1880) spongy particles. There are, however, a number of cognate properties possessed by wet clays which are of assistance in the clarification of our concept of plasticity. For example, the slow development of plasticity during the weathering or aging of clays; the action on clay-slip of alkalies, hydrolysable salts, acids, and certain organic compounds like tannin; the high tenacity of dried clays, etc.

The facts connected with the action of alkalies, etc., on clay-slip have been worked out by many investigations on the sedimentation of clay, etc., suspended in water. It has been observed that there are three classes of substances concerned in these effects:—

I. *Flocculation.*—Acids, acid salts, lime, calcium sulphate, sodium chloride, and most neutral salts cause the fine particles in suspension to flocculate or coagulate into groups and settle. Some of these agents also enhance the plasticity of clays.

II. *Deflocculation.*—A small proportion of ammonia, alkali hydroxide, alkali carbonate, borate, silicate, or a salt of other weak acids deflocculate, de-coagulate, or peptise the clay causing it to assume a more finely divided condition than in water, and thus remain in suspension for a longer period. These agents also diminish the plasticity of clays.

III. An excess of the deflocculating agents may produce the converse effect giving the same result as if an acid had been added.

The attractive forces exerted on the molecule at the surface of a liquid are smaller than on a molecule in the interior so that there is a tendency for the surface molecules to move inwards. The general result is that the surface tends to contract so as to leave the smallest number of molecules on the surface. K. Fuchs (1889), M. Whitney (1892), and W. J. A. Bliss (1895) have pointed out that with fine-grained particles of a solid suspended in a liquid there are two cases:—

(1) The molecules of the solid attract those of the liquid more strongly than they attract one another and more strongly than the molecules of the liquid attract one another. In that case the water film about the particles will tend to enlarge, and the grains will not come together, but rather be held apart. The system will be in equilibrium when each particle of the solid is surrounded by a shell of liquid nearly the same thickness as the radius of intermolecular attractive forces. The particles will then repel one another if brought closer together than twice the radius of the molecular force. This corresponds with the phenomenon of deflocculation.

(2) If the attractive force of the liquid for the liquid is greater than that of the solid for the liquid, the particles will tend to approach closely to one another. Otherwise expressed, the fine-grained particles of the suspended solid will flocculate.

The effect of alkalies is to keep the clay particles apart, the effect of acids is to make them form aggregates. The result is rather remarkable. Clay-slip prepared with about 0·3 per cent. of a mixture of sodium carbonate and silicate, can be readily poured in casting operations, and yet it contains less water than a stiff mass of clay without the alkali. The addition of a little acid to the former so as to neutralise the alkali is attended by an immediate "solidification" of the slip. The vessel can then be turned upside down without interfering with the contents. The addition of more alkali will again make the slip pour readily. These properties are extensively utilised in the ceramic industries.

Let F_{sl} denote the attractive force of the solid for the liquid, and F_{ll} that of liquid for liquid, then flocculation or deflocculation will occur according as $F_{sl} - F_{ll} = F$ is negative or positive. If F decreases there is an increasing tendency to flocculation. The gravitational attraction of the particles for one another may be assumed constant so that when a change is made in the composition of the liquid, by the introduction of dC parts of a solute, $\frac{dF}{dC}$ will be negative when a trace of a flocculating substance (Class I.) is added; and positive when a trace of a deflocculating substance (Class II.) is added. $\frac{dF}{dC}$ changes sign for substances in which there is a reversal of the effect when increasing proportions of the solute are added (Class III.). In all cases therefore $\frac{d^2F}{dC^2}$ is negative.

Attempts to evaluate F_{ll}, the attraction of two unit masses of a solution have been made by S. D. Poisson (1831), P. Volkmann (1882), O. E. Meyer (1861), W. J. A. Bliss (1895), and W. Sutherland (1893); and the effect has been studied by D. Berthelot (1898), and B. Galitzine (1890). J. J. Thomson (1888) showed that the value of F_{ll} is probably slightly greater near the solid than in the same portion of the solution further away, and is different from the value at the boundary surface between the liquid and air. Consequently, F_{sl} may be qualitatively but is not quantitatively proportional to the surface tension of the liquid. The value of F_{sl}, the attraction of unit mass each of solid and liquid, has not been determined experimentally, although W. J. A. Bliss suggested an expression analogous to that employed for F_{ll}.

To summarise, when the molecular attraction of the liquid for the liquid predominates over that of the clay for the liquid, the shell of liquid about the clay will diminish, and flocculation will set in. This case is characterised by acids and substances of Class I. When the molecular attraction of the clay for the liquid predominates over that of liquid for liquid, the shell of liquid about the clay will enlarge, and the grains of clay will be kept apart and deflocculation will occur. This case is typical of dilute solutions of the alkalies, and substances of Class II. The behaviour of substances in Class III. shows that there is a critical concentration below which the molecular attraction of clay for the liquid predominates, and above which the attraction of liquid for liquid is predominant. The gravitational attraction of solid for solid has been neglected because it can be regarded as a constant under these conditions. L. Wolf (1906) has built an explanation on the assumption that the particles of clay attract one another according to the gravitational law; but any other assumed law of attraction would apply equally well, or rather equally unsatisfactorily.

The hypothesis just indicated shows how the plasticity of a clay can increase with increasing proportions of water so long as the average thickness of the surface films of water on the particles of clay is not greater than average range of the molecular attraction of the clay for water. When enough water has been added to produce thicker films, part of the water will be outside the range of this attraction, and the clay will be less coherent, and become " sticky ".

The high molecular attraction of clay for water is illustrated by the magnitude of the Pouillet effect. With approximately the same surface area, the maximum effect with china clay is nearly 1·50 cals. per gram; 30·0 cals. with ground quartz; and 0·01 cals. with ground flint. Attempts by J. Aron, B. Kosmann, etc., to refer plasticity to the hydration of the clay molecules have not been very successful because no direct relation has been observed between the plasticity and the water of hydration *per se*. It is, however, noticeable that the greater the plasticity of the clay, the greater the proportion of water required to develop maximum plasticity.

Thus a highly plastic clay may take up 30 per cent. of water before becoming sticky, while less plastic clay requires 20 per cent., and a short clay may become sticky after 10 per cent. of water has been added.

In analysing the effect of acids, bases, and salts on clays, it is necessary to take adsorption into consideration. The relation of the clay particles to the liquid may be drastically modified when the clay particles contain adsorbed salts, acids, etc. This, however, does not effect the qualitative explanation of the effects just outlined; nor is it necessary to make any assumption as to the nature of the attractive forces.

9. The Action of Colloidal Matter on Clay.

The remarkable effects of gum and other mucilages in enhancing the plasticity of clay has been utilised by potters for an indefinitely long time. In 1903, E. C. Acheson patented the use of aqueous solutions of the tannins and gallotannins, *e.g.* decoctions of oak-bark, etc.; and in 1918 G. Keppler and A. Spangenberg patented the use of decoctions of humic acid, peat, etc. These plasticising agents probably act indirectly by adsorption. The clay particles adsorb the organic colloid, and judging by results this probably lessens F_{sl}, the molecular attraction between the particles and the surrounding liquid. The plasticity of china clays, practically free from organic matter, shows that adsorbed organic colloids are not the source of their plasticity.

Clays which have been sodden with ground waters rich in organic matter are usually highly plastic; and those clays which can be shown geologically to have been deposited in swamps and bogs, or which have been in contact with such waters, are always plastic unless other metamorphic changes have occurred. Many such clays, however, are not plastic when freshly dug, but they become plastic during weathering. When first mined some of the clays are hard, but if they be moistened and exposed to sunshine and frost they more or less quickly disintegrate and crumble to fine-grained plastic clays.

Clays which are allowed to stand for a long time in contact with moisture become more plastic, or, as the workmen express it, more "buttery". Clays which have been boiled with water also become more plastic. Clays prepared by fast processes—filter-press—are not so "buttery" as when prepared by a slower process—slip-kiln. China clays prepared by the elaborate, apparently primitive Cornish process are more plastic than when the process of de-watering the clay is accelerated by filter-press. There is thus an intimate connection between the plasticity of a clay and its past history with respect to water. All this looks as if the clay is being hydrated to form a colloid.

Attempts have been made to establish the colloidal theory of plasticity by adding artificially prepared colloids to feebly plastic clays. A. S. Cushman (1902), for example, found that when colloidal silica is added to such a clay, the air shrinkage and the tensile strength of the clay are increased, but not the plasticity; but with colloidal alumina, neither the air shrinkage nor the tensile strength were increased but the plasticity was augmented. F. F. Grout, however, pointed out that unlike the plasticity of clays, the plasticity acquired by the addition of colloidal alumina is lost when the clay is dried. Similar remarks apply to the colloids prepared by precipitation from a mixed solution of alum and water glass. If the plasticity of clays is due to the presence of a colloidal aluminosilicate, it is therefore necessary to assume that it is due to a form which has not yet been recognised. S. Kasai (1896) could find no colloidal clay in Zettlitz china clay.

10. ATTEMPTS TO ISOLATE L'ARGILE COLLOÎDE.

If clay, freed from soluble salts, be boiled with water and allowed to stand 24 hours, extremely finely-grained particles of solid will remain in suspension an indefinitely long time. The suspended clay can be isolated by evaporation, or by the addition of a trace of sodium chloride, lime-water, etc., which rapidly precipitates the suspended clay. The finest particles are invisible with a $\frac{1}{12}$-inch objective. The stuff obtained by evaporating the "clear" liquid from ball clay, is a deep brown, hard, horny mass resembling glue. It adheres tenaciously to the tongue, and, like glue, it swells enormously when wetted with water, and the wet sticky mass shrinks enormously and cracks when dried. Cornish china clay gave about 0·005 per cent., Devonshire ball clays about 0·05 per cent. It is doubtful if this product represents all the colloidal matter in these clays. Obviously the method of isolation would miss any colloidal matter which might be present as a coating on other grains. No difference could be detected in the plasticity of the clay from which *l'argile colloîde* had been removed. The properties of this colloidal matter simulate in a highly exaggerated form the behaviour of clays on drying, and I am inclined to think that the colloid plays an important part in the drying of clay. I cannot see that the "felting" action of the particles of the drying clay is an adequate explanation of the comparatively high tenacity of dried clays. The impermeability of wet puddled clay to water is also difficult to understand on the "felting" hypothesis.

THE DE-HYDRATION OF DRIED CLAYS.

(By J. W. Mellor, N. Sinclair, and P. S. Devereux.)

It is generally supposed that clay retains its combined water up to about 500°, and J. W. Mellor and A. D. Holdcroft (1912) showed that if the heating be conducted *in vacuo*, the water commences to be slowly evolved at much lower temperature, even before 300°. E. Löwenstein (1909) showed that if clay be kept for some time at 25° over sulphuric acid, part of the so-called combined water in clay: $Al_2O_3 . 2SiO_2 . 2H_2O$, is lost. N. Sinclair repeated these experiments about 1910, and P. S. Devereux about 1914. The experiments were interrupted by war-work.

Finely powdered samples of clay were dried over 25 per cent. sulphuric acid, and placed in dessicators containing sulphuric acid of different concentrations. The desiccator and contents were kept in a bath at a constant temperature of 25°. The samples were weighed every week until the readings appeared constant. The time occupied was approximately three months. If years were available, possibly more water would be lost by the clay. The different samples of sulphuric acid employed are indicated in Table II.

TABLE II.

VAPOUR PRESSURE OF AQUEOUS SOLUTIONS OF SULPHURIC ACID AT 25°.

Per Cent., H_2SO_4.	Vapour Pressure.
30	18·0
40	13·5
50	8·8
60	4·3
70	1·8
80	0·6
90	0·0

The following tables contain the observed results. Table II. is by Mr. Norman Sinclair, and Table IV. by Mr. P. S. Devereux.

TABLE III.

PERCENTAGE LOSS IN WEIGHT ON EXPOSURE OF DIFFERENT CLAYS IN DRIED ATMOSPHERES.

Per Cent, H_2SO_4.	Halloysite.	Pyrophillite.	Wetley Marl.
30	1·72	+ ·04	·76
40	8·68	·00	2·00
50	10·36	·20	1·32
60	11·40	·12	2·60
70	11·52	·24	2·80
80	12·52	·20	3·08
90	11·84	·40	3·20

The + symbol means that there is an increase in weight with the more dilute solutions of sulphuric acid. This is due to the adsorption of moisture. There is also evidence of a slight adsorption of a sulphur oxide with the more concentrated sulphuric acid.

TABLE IV.

PERCENTAGE LOSS IN WEIGHT ON EXPOSURE OF DIFFERENT CLAYS IN DRIED ATMOSPHERES.

Per Cent. H_2SO_4.	Ball Clay.	China Clay.	Glenboig Clay.	Halloysite.	Kaolinite.	China Clay.	Halloysite.
30	0·08	0·16	0·09	0·10	0·06	0·01	0·06
40	0·24	0·12	0·11	0·41	0·08	0·06	0·44
50	1·63	0·20	0·30	0·93	0·12	0·13	1·67
60	2·31	0·24	0·48	1·84	0·18	0·16	1·96
70	2·44	0·46	0·67	1·92	0·24	0·23	3·26
80	3·29	0·52	1·12	2·37	0·38	0·36	3·62
90	3·54	0·55	1·48	2·58	0·46	0·50	4·05

The three determinations of halloysite show different results, probably due to part of the assumed halloysite being china clay. The numbers for kaolinite refer to a well-crystallised sample from Glamorganshire investigated in another direction by J. W. Mellor and A. D. Holdcroft (1912). The results for ball clay, china clay, and one of the samples of halloysite are plotted in Fig. 4.

E. Löwenstein's observations are thus confirmed. Clays gradually lose some of their so-called combined water at ordinary temperatures. This water is reversible and is restored in a moist atmosphere, thus showing that no drastic change has occurred in the structure of the clay molecule. This change is totally different from that which occurs when water is expelled at the higher temperatures. E. Löwenstein believes that only one-fourth of the combined water is so expelled, but the action is so slow that this statement may require modification.

This over-dried clay, if such a term is applicable, has some important properties. The resorption of water is so very slow and it requires such a long time to restore the original plasticity, that the working qualities—plasticity, shrinkage, etc.—of certain troublesome clays can be mollified and regulated by desiccation. Mr. Bernard Moore tells us that this is a time-honoured custom in some branches of pottery manufacture and the subject has been discussed by A. V. Bleininger (1910). The dried clay approaches the condition of many unweathered fireclays in requiring exposure to a moist atmosphere for a long time before the original plastic condition is resumed. The custom of seasoning glass pots for a few months in a warm dry place may not really be so redundant an operation as might at first sight be supposed. From this point of view the storing of clays in a warm dry spot is not conductive to their subsequent working in their most plastic state.

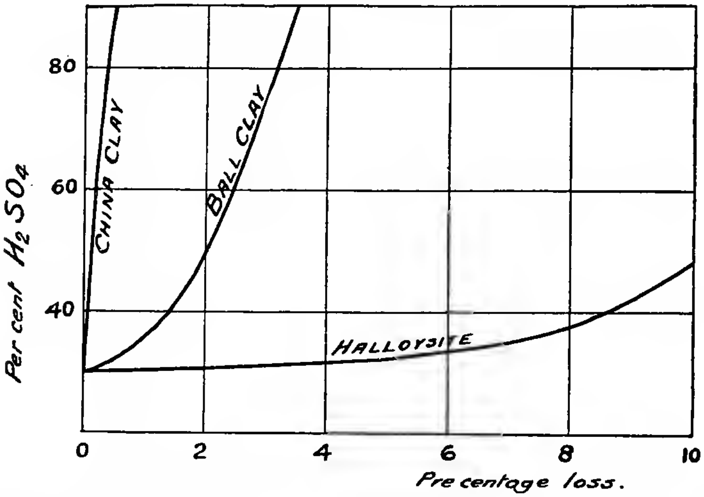

Fig. 4.—Loss in Weight of Clay when Confined over Sulphuric Acid of Different Concentrations at 25°.

DISCUSSION ON " COLLOIDAL PHENOMENA ".

The Chairman: As regards Professor Sven Odén's paper, he recalls an early investigation of my own in which I once put forward the theory that you can explain the properties of clay by appealing to the idea of the minuteness of the particles. I feel somewhat embarrassed that that investigation has been brought forward again under such distinguished patronage, because I had certainly come to feel very much that it did fail to explain the properties of the soils as we find them in the fields. I remember after the publication of the first edition of that first book of mine receiving a letter from Hillgard in California, in which he said: "If you had got the experience we have in this country of the soils and the soil areas formed in the valleys in some of our rivers, entirely formed by the washing down of finely powdered quartz from the gold mines, and noted the extraordinary physical behaviour of these soils, you would cease to believe that it is merely a question of fineness of grading to convert a quartz into a clay ". Later I had experience of certain soils in this country rich in fine silt particles which though heavy enough to be popularly called clays have an entirely different behaviour from typical clay soils. We get these very fine siliceous soils, which are not colloidal, if I may use this term to cover our ignorance. These soils slip abominably, but they do not flocculate and they cannot be brought into the tilth which characterises the true clay, such as is derived from the London clay. Again, the experience of workers like Mr. Robinson with the North Wales soils, and of the Scotch workers on their soils, where you do get soils which are largely recently powdered rock, show that there is, in these cases, a great absence of the typical clay properties. We have all of us during this discussion been warning one another as to the danger of working with material in which a great number of unknowns come into play. There is a great difference in what is called clay in different parts of the country merely because of the difference in rainfall and evaporation. Up in Scotland what my Aberdeen friends would call a thoroughly heavy working soil would, if transported down into Essex, be regarded as a light loam. Therefore, when we are correlating the laboratory with the agricultural standpoint we have got to be very guarded in our statements. None the less mechanical analysis enables us to define our terms and the classes of material we are dealing with; this at any rate is one factor among many, the resultant of which is the behaviour of the soil in the field. I sympathise entirely with Dr. Ormandy in his plea for working with pure materials and so getting our simple facts known; we have got to get the elements in the structure, knowing that the final result is a complex of a very great description.

Dr. W. R. Ormandy: I am going to ask your tolerance for a short time with reference to Professor Odén's paper. I am sure all of us who have to do measurements of the percentage of the various fineness of particles which are present in a suspension will give a tribute of thanks to

Professor Odén for having invented a method which at least can be carried out practically, but in so far as it is used for the measurement of the size of particles of clay, I would ask Professor Odén what he really is measuring. He is measuring a variable quantity. I have been working on the problem of endeavouring to get the average size of clay particles under various conditions for quite a long time, and Mr. Craven and I have tried the effect of treating clay with varying amounts of water under various conditions of agitation for different periods of time and we have done measurements of the particle size, both microscopically and otherwise. We found quite regular variations under any given set of conditions, but even the alkali from the glass produced measurable effects, and we found that it was necessary to work with quartz to eliminate the errors arising from such alkali. Working in that way we have found that with ball clay and china clay, as two typical clays, the size of the particle is a function of the time that it is in contact with the water. It is also a function of the quantity of water that it is in contact with. In other words, it does appear that you can produce the same dispersive effect that you get in ten days' boiling with water, in an hour, by the addition of a very small amount of alkali, and it does rather appear as if the clay adsorbs the free ions which are present in small quantity in water. The percentage of free ions in water is very small, and therefore the time which occurs before actual contact takes place must be in itself very considerable. Therefore I ask the question, "What do you mean by the size of the clay particle?" You can only say that a clay has a particle of a certain size when it has been in contact with water a certain time at a certain temperature. The size of the clay particle is a function of these variables, and this instrument has given wonderfully accurate results when dealing with finely ground carborundum, which is a very inert material, or finely ground sand, but I am equally confident that you would get very variable results with Professor Odén's machine if your soil contained a large amount of clay. It would be dependent upon the length of time of contact and the amount of water, and whether you had absolutely pure distilled water, because the amount of alkali in distilled water is frequently quite considerable, especially when on distillation the first fraction is taken.

It is impossible at this hour of the evening to deal with a lot of points which Dr. Mellor has brought forward in his paper. I am disappointed, in the first place, that Dr. Mellor himself is not here to read the paper and more particularly that there is no time to deal with it because, although I have heard other views expressed, I think it is a wonderfully complete paper and deals with almost every possible aspect of the subject of plasticity regarded, perhaps, not from the point of view of the soil specialist but from the point of view of the physico-chemist.

Professor Sven Odén: What Dr. Ormandy now says about these clays, gives me a strong impression that he seldom gets what I have called the prime particle structure. That is to say, he very often has complexes. Then it is quite right with the aforementioned experiments, since it takes a long time for an alkali to resolve a complex into its prime structure. I have been very interested in this aspect of the question, and have published a special paper on the finding of a method of resolving *this* (sketch) aggregate into a prime structure; and I have also boiled with various alkali solutions for a few hours. I have a paper here[1] which I will present to Dr. Ormandy. At first I had the same experience as Dr. Ormandy, namely, that we get various curves under various conditions. I then specially studied the conditions for our Swedish clays with a view to getting this prime structure, but I am quite convinced that, with very old clays, such as china clay and such like, which have been subjected to thermal influence, there will occur difficulties other than those experienced with the clays of my own country. Perhaps, according to our Chairman's remarks, the clays in my country would not here be called clays at all, but we have quite a distinct meaning as to what we wish to designate, and I think we must use this term " clay " for all these soils that have very fine particles, and we must distinguish between different types of clays. One type is only powdered rock material and is quite different from the London clay, but I am of the opinion that we must apply the name clay to all of them, and then go into further details. It may be that the method I have described in the paper I have given to Dr. Ormandy will not do for his clays, and it may be impossible to use it for some other clays. Nevertheless, I think that the method is fairly good. I only ask those who are interested to go into the matter in more detail before criticising.

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[1] *Studien über Tone III. Bull. of the Geological Inst. of Upsala*, vol. 16.

At the conclusion of the Discussion votes of thanks were moved by the **President** and carried with acclamation to **Sir A. Daniel Hall** for having taken the Chair throughout the meeting and to the authors of the Papers, more particularly to **Professor Sven Odén** for his presence and for his several contributions to the various sections of the discussion.

The meeting adjourned at 10.30 p.m.

CAPILLARITY.

A GENERAL DISCUSSION.

An Ordinary Meeting of the Faraday Society was held jointly with the Manchester Literary and Philosophical Society at Manchester on Friday, February 11, 1921, to discuss the subject of Capillarity.

Sir Henry A. Miers, M.A., D.Sc., F.R.S., President of the Manchester Literary and Philosophical Society, introduced into the Chair **Professor Alfred W. Porter, D.Sc. F.R.S.,** President of the Faraday Society.

Professor A. W. Porter: It is a great honour to me to take the Chair at this meeting. It is not the first meeting that the Faraday Society has held in Manchester, but it is the first that it has held in conjunction with your Literary and Philosophical Society. We have met twice before—once in 1913 for discussion on corrosion of metals, and later on we had another discussion on electrical furnaces; both of these were very well attended. But it is of special interest to us to join your Society here for this meeting. I do not want to take up your time with general remarks. I will call on Dr. Ferguson to read the two papers by which he will open our discussion on Capillarity.

STUDIES IN CAPILLARITY.

I. Some General Considerations and a Discussion of Methods for the Measurement of Interfacial Tensions.

By Allan Ferguson, M.A., D.Sc., Department of Physics, Manchester College of Technology.

The series of experimental studies in capillarity to which this paper forms an introduction owes its immediate origin to the pressing necessity for reliable values for the surface tensions at liquid-gas surfaces, at solid-liquid surfaces, and at solid-gas surfaces. An equal need exists for a knowledge of the temperature coefficients of these quantities, and of the contact-angles of liquids with solids, a need which has grown with, and is further emphasised by the remarkable development during the last generation of colloid chemistry and physics.

The value assigned to a surface tension varies very greatly (see p. 374) with the experimental method employed, and while it is true that much excellent experimental work has been done, it is equally true that much of this work has suffered from a lack of co-ordination, and from a want of appreciation of the dynamical and mathematical principles involved. Indeed a large part of the recent work on surface tension is characterised by an accuracy of experiment which verges on the meticulous, accompanied by vague dynamical argumentation in which writers have been saved from serious mistakes of the hundred-per-cent. order only by a providential cancellation of errors.

Thus, in a recent study[1] of the surface tensions of water and of benzene in which the experimental work is of a very high order, the writers point out that the values of the surface tension of water as measured by the capillary-rise and the ripple method differ by as much as 4 per cent.—the deviation being due mainly to the fact that "the theoretical basis of some of the methods is not sufficiently exact".

Nevertheless, the same writers, in discussing the drop-weight method, define an "ideal" drop as one whose weight is given by the equation

$$W = Mg = 2\pi rT \quad . \quad . \quad . \quad . \quad . \quad \text{(i)}$$

"the weight which the drop from any tip would have if Tate's law were valid". Tate,[2] I fear, never promulgated any such law, but contented himself with a simple statement of the proportionality between the weight of the drop and the radius of the tip from which it falls.

Equation (i), in fact, outrages elementary mechanical principles. It neglects the pressure-excess inside the drop due to curvature, and it would be far more reasonable to define the ideal drop by the equation :—[3]

$$Mg = \pi rT.$$

The error is a common one, and is to be found in most manuals of physical chemistry, although the correction was given a generation ago by Worthington.[1] Fortunately, one is generally concerned in experimental work with ratios of drop-weights, and the peccant 2 disappears on division.

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[1] *Jour. Amer. Chem. Soc.*, **41**, 499 (1919). [2] Tate, *Phil. Mag.*, **27**, 176 (1864).

[3] See *e.g.* Poynting and Thomson, "Properties of Matter" (1902), p. 161.

Again, Coombs and Richards,[2] in a careful determination of the surface tension of water and of benzene, have indulged in what the late Lord Rayleigh termed some "mild reflections on the inadequacy of the help afforded by mathematics," in the elucidation of capillary problems.[3] Their criticism takes a curious form, inasmuch as the canon of acceptance or rejection of a particular approximation appears to depend on whether the approximation does not, or does give impossible values when used outside the range for which the approximation is valid. Such a canon would make very short work of the binomial theorem for fractional indices!

It seems very necessary, therefore, to show exactly what problems have been solved mathematically, under precisely what circumstances the approximations given are valid, and in what problems there is a difference of opinion as to the validity of the solutions that have, from time to time, been propounded.

This apart, I desire here briefly to discuss the various known methods for the measurement of capillary constants, and to consider which of them may most usefully be employed in the measurement of interfacial tensions. There is little need to enlarge on the importance of an *accurate* knowledge of the tension at a liquid-liquid interface—the necessity is known—urgent, and the values of the existing figures, determined as they often are by the aid of stalagmometers, visco-stalagmometers, and other instruments of hybrid derivation and of doubtful accuracy, are open to more than a little suspicion.

At the outset I have mentioned the lack of co-ordination of the existing work. The need for an ordered determination of constants is pressing, and it would seem that much of the careful work already done is in measure wasted, not so much by overlapping, for within limits a certain amount of overlap is all to the good, as by the use of different methods whose relative accuracy has not been sufficiently well estimated, and, in some cases, by lack of appreciation of the help which has undoubtedly been given by mathematics.

Without venturing to lay down cast-iron rules, I here give an outline of a systematic attack on the problem, which would have been carried farther during the last year, had the work not suffered interruption by the heavy demands due to the unprecedented influx of students into this, as into other teaching institutions. Briefly outlined, the scheme of work stands as follows:—

(α) General considerations, with a review of those methods which are most likely to prove suitable for the measurement of interfacial tensions.

(β) Improvements in the capillary-rise method.

(γ) An experimental study of the limits of accuracy of Jaeger's method.

(δ) A comparative experimental study of the other principal methods, elucidating the sources of error in, and the consistency of these methods.

(ε) The development of methods suitable for the measurement of
  (i) Interfacial tensions,
  (ii) The surface tensions of substances only obtainable in small quantities, and of substances such as molten metals,

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[1] *Proc. Roy. Soc.*, **32**, 362 (1881).

[2] *Jour. Amer. Chem. Soc.*, **37**, 1643 (1915).

[3] *Proc. Roy. Soc.* (A), **92**, 184 (1915-16).

    - (iii) Contact angles.
- (ζ) The systematic measurement of
    - (i) The surface tensions of selected classes of organic compounds, paying special attention to temperature coefficients,
    - (ii) Interfacial tensions,
    - (iii) Contact-angles of liquids in contact with glass and with other solids.

The present paper deals with the first section of the above scheme, and the paper immediately following describes certain improvements in the capillary-rise method which, without loss of accuracy, considerably simplify its technique.

Much difference of opinion exists concerning the reliability of the "Jaeger" method for the measurement of surface tensions. The method, as is well known, depends on the measurement of the maximum pressure required to release a bubble of air from a small capillary tube plunged vertically into the liquid under observation. Experiments are now in progress in which the extruded bubble is photographed under various pressures; the information thus acquired should serve as a criterion of the reliability of the method.

THE MEASUREMENT OF THE TENSION IN A LIQUID-GAS SURFACE.

Turn now to a brief consideration of the value of the various methods that have been proposed, from time to time, for the measurements of surface tensions. Some schematic form of set-out is necessary to avoid confusion, and the accompanying genealogical tree, whose structure explains itself, is perhaps as clear as any.

I do not propose to discuss these various methods at great length; I have, in another paper,[1] attempted some estimate of their relative value, and in a recent number of *Science Progress*[2] a very detailed analysis of the capillary-rise and of the drop-weight method has been given.

Generally speaking, one can say that the methods classified under the grouping (B) should in no case be employed unless one has sound independent evidence that the contact angle is either zero, or so small that its neglect introduces no appreciable error into the observed value of the surface tension.[3]

It is to the methods classified under the heading (A) that we must turn to find our ideal method, and of these (7), (4) and (10) promise very well. From my own experience, I incline to say that any of these three methods will give good results, and Jaeger's method is particularly convenient in practice. The maximum pressure-excess can be very exactly measured, and temperature control is relatively easy. It is not sufficiently clearly realised that the method yields absolute and not comparative values, and a certain suspicion appears to exist that the experimental conditions do not approximate closely enough to a statical state. These doubts I hope to settle by the experiments previously mentioned.

Method (4) too, is very convenient and exact if the conditions of the theory are properly observed. By bending a thin rod into a circle of large radius an anchor ring is formed, and suspended by three threads from a balance pan so that its plane is horizontal. If the ring be allowed to touch the surface of a vessel containing liquid and be then withdrawn, a distinct

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[1] Ferguson, *Science Progress*, Jan. 1915, p. 428.

[2] Oct. 1920, p. 223.

[3] The neglect of a contact angle of 8° introduces a 1 per cent. error into the value of T.

METHODS FOR MEASURING SURFACE TENSION

- (A) Independent of contact-angle
  - Vibrations
    - (1) Vibrations of drop
    - (2) Waves on jet
    - (3) Ripples
  - Balance methods
    - (4) Pull on ring
    - (5) Tension in film
  - Bubbles and drops
    - (6) Pressure in pendent drop
    - (7) Large bubbles and drops
    - (8) Bubbles and drops (any size)
  - Capillary tubes
    - (9) Sentis' method
    - (10) Jaeger's method
- (B) Dependent on contact-angle
  - Capillary rise
    - (11) Capillary tube
    - (12) Capillary plates:
      - (*a*) parallel
      - (*b*) inclined
    - (13) Single plate
    - (14) Large cylinders
  - Balance methods
    - (15) Wilhelmy's method
    - (16) Pull on sphere
    - (17) Pull on disk
    - (18) Buoyancy method
  - Bubbles and drops
    - (19) Total depth of large bubbles and drops

(20) (Unclassified) Drop-weight method.

maximum pull is observed, and the surface tension of the liquid can be accurately calculated in terms of the maximum pull and the dimensions of the ring. The method might with advantage be much more widely used, as the weighings can be made accurately, and temperature control is not too difficult.

Of the methods included under the general heading B, it is worth noting that (12*b*) has recently been recommended as a working practical method.[1] Two vertical plates inclined at a small angle are dipped into the liquid under examination, and the angle between the plates is varied until the surface of the liquid between them coincides with one of a series of confocal hyperbolas drawn on one of the plates.

A simple and rapid way of roughly measuring the surface tension of very small quantities of liquids is indicated by Kiplinger.[2] A short column of the liquid is introduced into a capillary tube of known bore which is then tilted until the meniscus at the lower end becomes plane. The surface tension readily follows from a knowledge of the angle of tilt. The results are uniformly 3 or 4 per cent. too low.

Of the various balance methods classified under (B), I have found the measurement of the surface tension pull on a sphere suspended beneath a balance pan very convenient and sensitive.

If the surface tension pull on such a sphere of radius R is equivalent to a force of mg dynes, then it can be shown that[3]

$$m = 4\pi\rho a^2\left\{R - \frac{\sqrt{a}R}{3} - \frac{a}{3}\right\},$$

an equation which can conveniently be solved for a^2 by successive approximations. With a sphere of glass just under 6 inches in diameter ($R = 7{\cdot}321$ cm.), and water as the test liquid, the value of m is about 6·35 gms., and, as far as the weighings are concerned, it is quite easy to obtain T to 1 part in a thousand.

The mean of 17 independent readings on different samples of water gave, on reduction to 15° C,

$$T_{15} = 73{\cdot}45 \pm 0{\cdot}023 \frac{\text{dynes}}{\text{cm.}}.$$

It may be useful to give here a table of some of the later values obtained for the surface tension of water. The varying values obtained

T_{15}.	Observer.	Method.
73·26	Volkmann	Capillary-rise.
73·46	Domke	Capillary-rise.
73·72	Dorsey	Ripples.
73·45	Hall	Weighing tension in film.
73·76	Sentis	Capillary tubes.
74·22	Watson	Ripples.
73·45	Ferguson	Pull on sphere.
74·30	Pedersen	Waves on jet.
72·78	Bohr	Waves on jet.
74·22	Kalähne	Rippled surface used as diffraction grating.
73·38	Richards and Coombs	Capillary-rise.
73·88	Ferguson	Jaeger's method.
73·55	Brown and Harkins	Capillary-rise.

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[1] Grummach and Bein, *Zeit. Instrumentenk*, June, 1919, p. 195; *Sci. Abs.* A., **22**, 500, 1919.

[2] *Jour. Amer. Chem. Soc.*, **42**, 472, 1920.

[3] Ferguson, *Phil. Mag.*, Nov. 1913, p. 925.

serve to emphasise the difficulties inherent in the subject. Personally, I am convinced that the most potent factor in producing this variation is the difficulty of preparing a perfectly pure substance (or surface). The exact conditions under which the various mathematical approximations hold good are well known, and, *provided these conditions are fulfilled*, the approximations provided will represent the experimental results with more than sufficient accuracy. But the only satisfactory way of settling this point is to undertake the research outlined under the heading (δ) above.

MATHEMATICAL PRINCIPLES.

The evidence above detailed indicates that a considerable confusion exists as to what problems have been, and what have not been exactly solved; and that where the problem is incapable of exact solution, needless doubts have arisen concerning the value of the approximations given, and the conditions under which the approximations hold good. I propose, therefore, in this section, to devote some little space to a discussion of the more important of these problems, and I hope to show that, even in those cases which are usually considered to require complex analysis, second order corrections may be reached by the aid of very simple mathematics, involving nothing more recondite than a few standard differentiations and integrations.

We shall take it for granted that, across any line of length ds drawn in the surface of liquid there is exerted a tension Tds, whose direction is normal to the line, and in the tangent plane to the surface. The quantity T is called the *Surface Tension* of the liquid, and is reckoned, in C.G.S. units, in dynes per centimetre (or grams per second per second).[1] Further, if R_1 and R_2 are the principal radii of curvature at any point of a curved surface in which there exists a surface tension T, then the pressure excess on one side of the surface over that on the other side is given by

$$p = T\left(\frac{1}{R_1} + \frac{1}{R_2}\right).$$

This is the well-known equation[2] whose solution has, from time to time, engaged the attention of most of the famous analysts of the nineteenth century. Briefly,[3] we may summarise the results of their work in the statements that (1) an exact solution of the equation in its most general form cannot be attained; (2) that even if we confine ourselves to the case in which the surface is one of revolution we can obtain approximate solutions only in certain special cases; and (3) that *exact* solutions may be found in those cases where one of the principal radii of curvature becomes infinite. This is the case contemplated when a liquid rises (or is depressed) between two parallel plane surfaces held closely together, or when a liquid is in contact with a plane vertical wall.

The cases which come under the heading (2) are of most importance from our point of view, and we shall study, in some little detail, the solution of the equation when the surface is one of revolution about a *vertical* axis. Two special cases concern us most closely—(α) the shape of the capillary surface inside a *small* vertical capillary tube, or, what amounts to the same thing, the shape of the outline of a *small* pendent drop of liquid, and (β) the shape of the capillary surface formed when a *large* bubble of air is imprisoned under the surface of a liquid or when a *large* drop of mercury rests upon a solid surface.

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[1] *Not* in dynes—an unfortunately common statement.

[2] For a simple proof, see Poynting and Thomson, "Properties of Matter," Chap. XIV.

[3] The discussion following is restricted to the capillary surface under gravity,

It is of the very first importance that we should attach clear ideas to the terms *large* and *small* contained in the preceding sentence.

Introducing the idea[1] of the "specific cohesion" a^2, we may say that a small capillary tube is one in which $\frac{r^2}{a^2}$ is small compared with unity. Or, since $2a^2 = rh$ very approximately, we may put the statement in equivalent form by saying that $\frac{r}{h}$ shall be small compared with unity. It must be very carefully remembered, therefore, that the smallness of a capillary tube is not an absolute thing, but is relative to the magnitude of the surface tension to be measured.

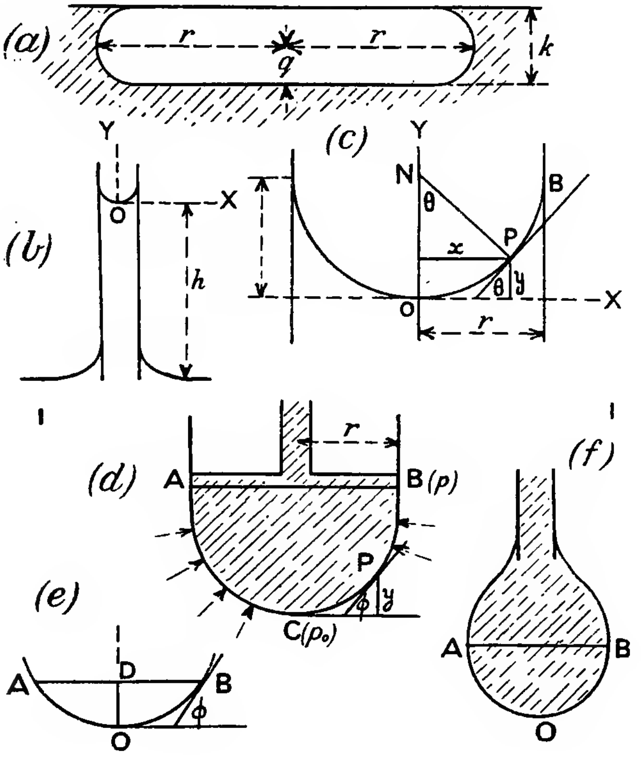

FIG. 1.

Similarly, where r is the radius of maximum section of a drop or bubble, the drop is considered to be large when $\frac{a^2}{r^2}$ is small compared with unity. If q be the vertical distance between the plane surface of the drop or bubble and the plane of greatest horizontal section (see Fig. 1 a), then, as we shall see, q is of the order of magnitude of a, and the condition implied is that $\frac{q^2}{r^2}$ is small compared with unity.

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[1] a^2 is *defined* by the identity $a^2 \equiv \frac{T}{g\rho}$ so that a has the dimensions of a length. As is well known, for liquids of *zero* contact angle, a first approximation to T is given by $T = \frac{1}{2}rh\rho g$, where h is the height to which the liquid rises in a capillary tube of radius r. Consequently $2a^2$ is of the order rh. Some writers (*Jour. Amer. Chem. Soc.*, 41, 520 (1919)) apparently use the equation $2a^2 = rh$ to *define* a^2, and then deduce the identity given above. This is quite incorrect.

It must be clearly understood, then, that the equations developed apply, and only apply, when these conditions are fulfilled; and that the failure of the equations outside these limits affords no reason for scepticism as to their reliability inside the limits.

We shall now proceed to develop in as simple a manner as possible the equation of the meridional curve of the surface inside a small vertical capillary tube; the argument will be given for a liquid of zero contact angle—its extension to a liquid of finite contact angle presents no special difficulty.

Let Fig. 1 b represent the liquid in its tube, and Fig. 1 c an enlarged diagram of the surface. With axes OX and OY as shown the pressure-excess on the two sides of the surface at P is given (i) by $T\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$ and (ii) by $g\rho(y + h)$. Equating these values, we have, where $a^2 \equiv \frac{T}{g\rho}$

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{y + h}{a^2}.$$

Now R_1 is the radius of curvature at P of the curve AOB, and R_2 is the length PN of the normal at P intercepted by the axis. Hence the above equation becomes[1]

$$\frac{1}{x}\frac{d}{dx}(x \sin \theta) = \frac{y + h}{a^2} \quad . \quad . \quad . \quad . \quad (i)$$

Innocent as this equation may appear, its exact solution is, apparently, impossible. Approximate solutions have been given by many analysts[2] by more or less complex methods; I shall here attempt to outline a process which will give us the second order correction in a relatively simple way.

In principle the method consists in working out an approximate value for y; this approximate value, substituted in equation (i), now makes it

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[1] For (see any text-book on the differential calculus),

$$\frac{1}{R_1} = \frac{d\theta}{ds} = \frac{d\theta}{dx} \cdot \frac{dx}{ds} = \frac{d\theta}{dx} \cos \theta.$$

And, from Fig. 1 c

$$\frac{1}{R_2} = \frac{\sin \theta}{x}.$$

Hence

$$\begin{aligned}\frac{1}{R_1} + \frac{1}{R_2} &= \frac{1}{x}\left(x \cos \theta \frac{d\theta}{dx} + \sin \theta\right) \\ &= \frac{1}{x}\left(x \frac{d(\sin \theta)}{dx} + \sin \theta \cdot \frac{dx}{dx}\right) \\ &= \frac{1}{x}\frac{d(x \sin \theta)}{dx}.\end{aligned}$$

[2] Laplace, "Mécanique Céleste," Supp. au X^e Livre (1805). Poisson, "Nouvelle Théorie de l'Action Capillaire (1831), Chap. IV. Mathieu, "Théorie de la Capillarité" (1883), Chap. II. Rayleigh, *Proc. Roy. Soc.* (A), 92, 184 (1915). Lohnstein, *Wied. Ann.*, 54, 713 (1895).

immediately integrable. Integrating, we develop a more accurate value of y, which is again substituted in equation (i). The process may be repeated again and again, the limit depending mainly on the patience of the operator.

A first approximation to the value of y may be worked out by a method which is a simple modification of that originally used by Laplace. This value is determined quite simply by Mathieu[1] and by Minchin,[2] and the approximate value of y is

$$y = c - \sqrt{c^2 - x^2} + \frac{c^3}{3a^2} \log_e \frac{c + \sqrt{c^2 - x^2}}{2c} \quad . \quad . \quad \text{(ii)}$$

where c is a constant to be determined. In a liquid of zero contact angle, when $x = r$, as at B (Fig. 1 c), $\frac{dy}{dx}$ is infinite. Differentiating (ii) and putting $\frac{dy}{dx} = \infty$ when $x = r$, we see that $c = r$, and therefore

$$y = r - \sqrt{r^2 - x^2} + \frac{r^3}{3a^2} \log_e \frac{r + \sqrt{r^2 - x^2}}{2r} \quad . \quad . \quad \text{(iii)}$$

where r is the radius of the capillary.

Now substitute this value of y in equation (i), and we have

$$a^2 \, . \, d(x \sin \theta) = \left(h + r - \sqrt{r^2 - x^2} + \frac{r^3}{3a^2} \log_e \frac{r + \sqrt{r^2 - x^2}}{2r}\right) x dx$$

or, integrating,

$$a^2 x \sin \theta + \mathrm{K} = (h + r)\frac{x^2}{2} - \int x \sqrt{r^2 - x^2} dx + \frac{r^3}{3a^2} \int x \log \frac{r + \sqrt{r^2 - x^2}}{2r} dx.$$

The two integrals are readily evaluated, giving

$$a^2 x \sin \theta + \mathrm{K} = (h + r)\frac{x^2}{2} + \frac{(r^2 - x^2)^{\frac{3}{2}}}{3} + \frac{r^3}{3a^2}\left[\frac{x^2}{2} \log \frac{r + \sqrt{r^2 - x^2}}{2r} + \frac{1}{4}(r - \sqrt{r^2 - x^2})^2\right] \quad \text{(iv)}$$

From Fig. 1 c, we see that x and θ vanish together so that, from (iv), $\mathrm{K} = \frac{r^2}{3}$. Also when $x = r$, $\sin \theta = 1$, and (iv) becomes

$$a^2 r = (h + r)\frac{r^2}{2} - \frac{r^3}{3} + \frac{r^3}{3a^2}\left[\frac{r^2}{2} \log_e \tfrac{1}{2} + \frac{r^2}{4}\right],$$

or

$$2a^2 = rh + \tfrac{1}{3}r^2 - \frac{r^4}{6a^2}(2 \log_e 2 - 1) \quad . \quad . \quad . \quad . \quad \text{(v)}$$

Approximately,

$$2a^2 = rh + \tfrac{1}{3}r^2,$$

and this value, substituted in the small term on the R.H.S. of (v) gives, after a few simple reductions

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[1] Mathieu, *l.c.*, p. 45.

[2] Minchin, "Hydrostatics" (Oxford, Clarendon Press, 1892), p. 360.

$$2a^2 = rh\left[1 + \frac{1}{3}\frac{r}{h} - \frac{r^2}{3h^2}(2\log_e 2 - 1) + \frac{r^3}{9h^3}(2\log_e 2 - 1)\right]$$

$$= rh\left(1 + \frac{1}{3}\frac{r}{h} - 0{\cdot}1288\frac{r^2}{h^2} + 0{\cdot}0429\frac{r^3}{h^3}\right) \quad . \quad . \quad . \quad . \quad . \quad \text{(vi)}$$

Now consider the results obtained by more complex methods of analysis. Poisson[1] gives, in effect

$$2a^2 = rh\left(1 + \frac{1}{3}\frac{r}{h} - 0{\cdot}1288\frac{r^2}{h^2}\right).$$

By a very much longer analysis, Rayleigh[2] has obtained a third-order correction, his value being

$$2a^2 = rh\left(1 + \frac{1}{3}\frac{r}{h} - 0{\cdot}1288\frac{r^2}{h^2} + 0{\cdot}1312\frac{r^3}{h^3}\right) \quad . \quad . \quad \text{(vii)}$$

and it will be seen that equation (vi), which only professes to be accurate as far as the term in $\frac{r^2}{h^2}$ inclusive, differs very little numerically from Rayleigh's equation.

An interesting and simple way of approximating to the correction terms was first given, apparently by Desains, who treated the meridional curve as elliptical. One way of arriving at the correction terms on this assumption is given by Mathieu[3] and by Rayleigh,[4] but it can be exhibited in a much more simple and direct way as follows:—

Consider the outline in Fig. 1 (*b* and *c*) as the outline of a semi-ellipse of semi-axes r and b. Then, equating $2\pi r\mathrm{T}$ to the weight of liquid raised (including the weight of the liquid in the meniscus) we have,

$$2\pi r\mathrm{T} = \pi r^2 h\rho g + \tfrac{1}{3}\pi r^2 b\rho g$$

or,

$$2a^2 = rh + \tfrac{1}{3}rb \quad . \quad . \quad . \quad . \quad . \quad \text{(viii)}$$

But, where R is the radius of curvature at the origin O, we have *accurately*

$$2a^2 = \mathrm{R}h,$$

and R, the radius of curvature at the end of the semi-axis minor of an ellipse is equal to $\frac{r^2}{b}$.[5] Hence

$$2a^2 = \frac{r^2}{b}h \text{ or } b = \frac{r^2 h}{2a^2},$$

which value of b, substituted in (viii) gives

$$12a^4 - 6rha^2 - r^3h \doteq 0.$$

Solving this as a quadratic in $2a^2$, we obtain

$$2a^2 = \frac{1}{6}\left[3rh + 3rh\left(1 + \frac{4}{3}\frac{r}{h}\right)\right].$$

On expanding the surd, we have finally

$$2a^2 = rh\left(1 + \frac{1}{3}\frac{r}{h} - 0{\cdot}1111\frac{r^2}{h^2} + 0{\cdot}0741\frac{r^3}{h^3}\right) \quad . \quad . \quad \text{(ix)}$$

giving value of a^2 in very close numerical agreement with (vi) and (vii).

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[1] "Nouvelle Théorie . . ." (1831), p. 112.

[2] Rayleigh, *l.c.*, p. 189.

[3] Mathieu, *l.c.*, p. 49.

[4] Rayleigh, *l.c.*, p. 190.

[5] See any text-book on the differential calculus.

The equation

$$2a^2 = rh\left(1 + \frac{1}{3}\frac{r}{h} - 0{\cdot}1288\frac{r^2}{h^2}\right) \quad . \quad . \quad . \quad \text{(x)}$$

is amply accurate for experimental purposes, and may be used with complete confidence in the determination of T for liquids having surface tensions of the order 30 $\frac{\text{dynes}}{\text{cm.}}$, and tubes of 1 mm. (or less) bore. Thus, to fix our ideas, consider a liquid of surface tension 30 $\frac{\text{dynes}}{\text{cm.}}$ and density 0·8 $\frac{\text{gms.}}{\text{c.c.}}$. Such a liquid, if its contact angle were zero, would rise to a height of about 1·5 cm. in a tube of 1 mm. bore. The correcting terms in (x) for this liquid would then be

$$\frac{1}{3}\frac{r}{h} = \frac{1}{3} \times {\cdot}0333 = 0{\cdot}0111, \quad 0{\cdot}13\frac{r^2}{h^2} = 0{\cdot}13 \times {\cdot}00111 = 0{\cdot}0001,$$

and the term in $\frac{r^3}{h^3}$ is quite inappreciable.

Now consider the case of a large drop of liquid sessile on a horizontal surface, or a large bubble of air imprisoned under a sheet of glass. The equations appropriate to such a system are

$$2a^2 = q^2 - \frac{2a^3}{3r}(4 - \sqrt{2}) \quad . \quad . \quad \text{(xi)}$$

and

$$k^2 = 4a^2 \sin^2\frac{\omega}{2} - \frac{8a^3}{3r}\left(1 - \cos^3\frac{\omega}{2}\right) \quad . \quad . \quad . \quad \text{(xii)}$$

where r, q, and k have the meanings given by Fig. 1*a*. It is clear that the correcting terms in these equations are of the order $\frac{a}{r}$, and that therefore the size of the bubble or drop should be so chosen that $\frac{a^2}{r^2}$ is negligible in comparison with unity. In the case of water, for example, for which a^2 is about 0·075 sq. cms., a *radius* of 2½ to 3 cm. is the very smallest that can safely be employed. Mr. Langmuir, in some interesting experiments recently carried out on the contact angles of water drops,[1] has used drops varying from 0·7 to 1·25 cm. in radius, calculating the contact angle from the equation—

$$k^2 = 4a^2 \sin^2\frac{\omega}{2}$$

in which even the first order correction term of (xii) is neglected. For a drop 1 cm. in radius $\frac{a}{r}$ in the case of water is about 0·27 and $\frac{a^2}{r^2}$ about 0·075, and neither of these quantities can be called small in comparison with unity. It would be far safer to use larger drops, measure both q and k independently, and so obtain the values of a and ω for the actual drop or bubble under investigation. Such a procedure involves no special difficulties, and the necessary observations may be made either photographically or by cathetometer measurements.[2]

I do not propose to discuss here the development of equations (xi) and

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[1] *Trans. Faraday Soc.*, XV., June, 1920, p. 62.

[2] Magie, *Phil Mag.*, Aug., 1888; Ferguson, *ibid.*, April, 1913, p. 507.

(xii). In the paper just cited I have given a simple investigation of the problem[1] which is conducted on principles similar to those laid down for the capillary tube problem. The analysis of the anchor ring problem[2] (number 4 in the "genealogical tree") follows much the same lines as the large bubble problem, and the approximations involved are of the same order.

THE MEASUREMENT OF THE TENSION IN A LIQUID-LIQUID SURFACE.

This problem is, for the colloid chemist, one of pressing importance, and the attempts made, up to the present, to forward its solution are of very doubtful value. The discussion of the agreement between theory and experiment in the case of the Gibbs-Thomson adsorption formula is pointless unless we have an experimental method which is above suspicion. At present the agreement is apparently considered good if the observed and calculated results differ by less than 100 per cent., while some substances may show adsorption from 20 to 100 times greater than that calculated from the formula.[3] It is sheer waste of time to discuss reasons for these differences so long as the experimental methods are open to suspicion.

The great majority of the figures for interfacial tensions are obtained by some modification of the drop-weight method, in which, instead of finding the weight of a given number of the drops, one determines the number of drops formed by a given quantity of liquid.

Let Fig. 1 *d* represent a drop of liquid of density ρ, pendent, in another liquid of density ρ', from a tube of radius r. The drop is conventionally assumed cylindrical at AB. The equation of equilibrium of the portion ABCA is

$$2\pi r\mathrm{T} + \int_0^r (p_0 - g\rho' y)2\pi x\,dx = \left(p + \frac{\mathrm{T}}{r}\right)\pi r^2 + mg,$$

where p_0 is the pressure at c in the outer liquid. This leads at once[4] to

$$\pi r\mathrm{T} = mg\left(\frac{\rho - \rho'}{\rho}\right) \quad . \quad . \quad . \qquad \text{(xiii)}.$$

The theory is at best rough and ready. Moreover, the condition of drop detachment are very complex, and variations, when different pairs o liquids are concerned, are so pronounced, that it is difficult to recommend the drop method even as a comparative one. We shall do better to turn our attention to some of the other methods.

Of these, number (6) in our schematic set-out appeals very strongly. Suppose we form a drop of liquid in such a way that we can measure the vertical distance from any point of the drop surface to each of the free surfaces. We thus know the pressure difference (p) in the equation—

$$p = \mathrm{T}\left(\frac{1}{\mathrm{R}_1} + \frac{1}{\mathrm{R}_2}\right) \quad . \quad . \quad . \quad . \qquad \text{(xiv)},$$

and it remains to determine R_1 and R_2 at the point in question in order to obtain the value of T. R_1 and R_2 may be measured in several ways.

(1) We may use numerical methods for the solution of the differential

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[1] *L.c.*, pp. 508 *seqq.*

[2] Cantor, *Wied. Ann.*, 47, 399 (1892).

[3] Willows and Hatschek, "Surface Tension and Surface Energy" (*Churchill*, 1919), pp. 51 *seqq.*

[4] See also Lewis, *Phil. Mag.*, April, 1908.

equation. The method of Bashforth and Adams[1] consists in "developing the increments of the co-ordinates in series proceeding according to ascending powers of the increment of the quantity chosen as independent variable," and is accurate, but laborious.

Runge[2] has also developed a numerical method for the solution of differential equations, which is, in effect, an elaboration of Simpson's Rule, and he has actually chosen the capillary equation as an example for solution. Picard, Heun, Kutta, and Piaggio, have each devised numerical methods for the solution of differential equations, and an excellent resumé of their work is given in the volume cited below.[3]

(2) We may modify some of the graphic methods for the solution of differential equations. The capillary equation has been treated graphically by Kelvin[4] and by Boys.[5]

(3) As the surface is one of revolution about the y-axis, we may assume an equation of the form—

$$y = ax^2 + bx^4 + cx^6 + \dots$$

The equation

$$y = ax^2 + bx^4,$$

fits the curve very well for some distance on each side of the vertex. Knowing the co-ordinates of a number of points on the curve, the constants a and b can be calculated by the method of least squares. These being known, the principal radii of curvature at any point can at once be calculated. I have in this way found the value $T_{11} = 73{\cdot}4$ dyne-cm.$^{-1}$ for a water-air surface.[6] At the vertex of the drop, of course, $R_1 = R_2$ and (xiv) takes on the simple form

$$p = \frac{2T}{R}.$$

(4) If the co-ordinates be determined with sufficient accuracy, we may use interpolation formulæ to determine $\frac{dy}{dx}$ and $\frac{d^2y}{dx^2}$ at any point. Knowing these differential coefficients, the values of R_1 and R_2 follow at once.[7]

The above method gives T in terms of the fundamental formula, and should, after a critical estimate has been made of the various methods for evaluating the radii of curvature, yield trustworthy results. It was proposed by me as a possible method for interfacial tensions over eight years ago,[8] and its use has also been recently advocated by Professor Boys.[9]

But cases may arise in which it is not possible to measure the distances to the free surfaces, and it is convenient to have a method by which T may be evaluated from measurements made on the drop alone. This may be accomplished in two ways:—

(*a*) If oil be floated on the surface of water contained in a large vessel, and a large funnel be inverted and dipped vertically into the oil so that its rim is almost on the interface, a beautiful, flat and stable bubble may be formed by blowing gently into the bubble by means of a spray bulb. This bubble may be photographed and the surface tension evaluated, using equations (xi) and (xii) suitably modified to fit the problem. By photographing an air-bubble blown in this way under water and measuring q and r, I found,[1] from equation (xi) $T_8 = 73{\cdot}7$ dyne-cm.$^{-1}$. No difficulty should be experienced in similarly photographing, say, oil-water bubbles.

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[1] "An Attempt to Test the Theories of Capillary Action" (Camb. Univ. Press, 1888).

[2] *Mathematische Annalen*, **46**, 175, 1895.

[3] Piaggio, "Elementary Treatise on Differential Equations," Chap. VIII. (Bell, 1920).

[4] "Popular Lectures and Addresses," vol. i., p. 31.

[5] *Phil. Mag.*, **75**, 36 (1893).

[6] Ferguson, *ibid.*, March, 1912, p. 417.

[7] For an elementary discussion, see Mellor, "Higher Mathematics . . ." (1905), p. 315.

[8] Ferguson, *Phil. Mag.*, March, 1912, p. 430.

[9] Boys, *Jour. Soc. Chem. Ind.*, March, 1920.

(β) With a bubble or drop of *any* size, a knowledge of the Cartesian co-ordinates of a large number of points on the contour enables one to determine T. For the equations of equilibrium of *any* portion of the bubble may be written down in a form which involves the integrals $\int xdy$, $\int x^2dy$ and $\int xydy$. By plotting curves between x and y, x^2 and y, and xy and y, these integrals may be evaluated by means of a planimeter. In this way [2] the equations of equilibrium of a lenticular portion of a small drop of water (the portion ADBOA of Fig. 1 *e*) for which AB was about 4 mm., DO about 1 mm., and the angle ϕ was 45°, yielded a value $T_{11} = 76{\cdot}5$ dyne-cm.$^{-1}$. The value is high, but not unreasonably so, considering the difficulties of the measurement. Better results would probably be obtained if similar measurements were made on the portion ABOA of a drop shaped as in Fig. 1 *f* for which $\phi = 90°$. The method should prove specially useful for the study of the surface tensions of molten metals, alloys, and the like.

I hope shortly to be able to discuss the results of experiments which will serve to exhibit the capacities of these various methods.

THE SURFACE ENERGY OF SOLIDS.

I do not propose here to do more than indicate one or two ways of accumulating data which may serve to evaluate these important constants.

Measurements of the surface tension in a solid-liquid surface have already been attempted. The solubility of a solid in a given solvent is a function of the dimensions of the solid particles, and changes by a measurable amount when the particles become very small. If s is the solubility for particles of radius r, and s_0 the solubility for "large" particles, then approximately

$$T = \frac{\rho r R\theta}{2} \log_e \frac{s}{s_0}.$$

In this way the surface tension at a barium sulphate-water surface has been found to be of the order 4000 dyne-cm^{-1}.

Similarly the surface tension in a solid-air surface might be measured by atomising and at the same time freezing a liquid. The vapour pressure outside these small particles would differ by a measurable amount from that outside a plane surface; the difference, which could be determined by known methods would serve to measure the surface tension of the solid.

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[1] Ferguson, *Phil. Mag.*, April, 1913, p. 517.

[2] *Ibid.*, p, 519.

STUDIES IN CAPILLARITY.

II. ON A MODIFICATION OF THE CAPILLARY TUBE METHOD FOR THE MEASUREMENT OF SURFACE TENSIONS.

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The determination of surface tensions by the measurement of the rise of a liquid in a capillary tube is more than ordinarily difficult. It is not easy, in the first place, to find a tube of sufficiently uniform cross-section to use with different liquids—some experimenters have spent as much as four months in searching for a uniform piece of capillary tubing.[1] When this is found, the calibrating, cleaning and keeping clean of such a piece of tubing are no small matters. Nor is it easy to measure the height of ascent of the liquid, and to estimate the temperature of the meniscus with the accuracy demanded. And when we remember that, all the measurements having been made with due care, the value obtained is not T, but $T\cos\theta$ it becomes increasingly clear that the convenience of this widely used method is more apparent than real.

The importance of a knowledge of the temperature-coefficient of a surface tension requires special emphasis. Not only does a knowledge of this coefficient enable us to make comparisons between different liquids under comparable temperature conditions, but it also enables us to calculate the critical temperature of an unassociated liquid with considerable accuracy. For the surface tension of such a liquid is expressed very closely, from freezing point to critical temperature, by the equation

$$T = T_o(1 - b\theta)^n$$

where b is accurately the reciprocal of the critical temperature.[2] The exactness with which this equation gives the critical temperature may be judged from the figures given in Table I. below.

TABLE I.

Substance.	$\theta_c\left(=\frac{1}{b}\right)$.	θ_c Observed.	Difference.
Ether . . .	194·0°	193·8°	+ 0·2°
Benzene	288·0°	288·5°	− 0·5°
Methyl formate . .	213·0°	214·0°	− 1·0°
Chloro-benzene . .	358·0°	359·2°	− 1·2°
Methyl butyrate . .	281·0°	281·3°	− 0·3°
Ethyl formate . . .	235·0°	235·3°	− 0·3°
Propyl formate . .	265·0°	264·9°	+ 0·1°

It is clear, then, that a few measurements of the surface tension of an unassociated liquid at fairly widely separated temperatures will enable us to calculate *b* and *n*, and will thus furnish us with a practical method for measuring its critical temperature.

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[1] Harkins and Brown, *Jour. Amer. Chem. Soc.*, 41, 503 (1919).
[2] Ferguson, *Phil. Mag.*, Jan. 1916, p. 37.

But these measurements demand an accurate knowledge of the temperature of the meniscus—a quantity by no means easy to determine, demanding, as it does, fairly elaborate thermostatic arrangements. Further than that, either expense must be incurred by closing the thermostat with windows of optical glass, or time must be spent in testing such pieces of glass as may be at hand.[1]

The importance of surface tension measurements in modern colloidal work renders it imperative to develop a method which shall be rapid, accurate, and shall not make too heavy a demand on the instrumental equipment of a technical laboratory. It is, we think, the unanimous opinion of workers in this branch of physics that the capillary-rise method is very difficult in practice, and is the reverse of rapid.

Practically all these troubles are swept away if, instead of measuring the rise of the liquid in a narrow tube, *we force the liquid down to the lower end of a tube immersed vertically therein, and measure, on a convenient manometer, the pressure required to effect this.*

Consider the advantages of such an arrangement:—

1. Calibration troubles are completely avoided. It is only necessary to measure, once for all, the bore at the end of a capillary tube of circular cross-section. This end is the position of reference for *all* liquids.

2. The capillary portion of the tube may be quite short, and the tube is consequently much more easily cleaned, and kept clean.

3. The thermostatic arrangements are much simplified. The liquid may be heated electrically, and temperatures taken by means of a fine thermo-couple placed quite close to the end of the capillary.

4. The use of the cathetometer is greatly facilitated. It is far easier to measure the difference of level of the surfaces of a liquid in the limbs of a pressure gauge than to measure the rise in a capillary tube. Moreover, any convenient manometer may be used—a point of importance in a laboratory where appliances are restricted. As is easily seen, if the lower end of the capillary be *just* touching the liquid under observation, and the same liquid be used in the manometer, the difference of level observed will be equal to the height to which the liquid will rise in the capillary tube in the ordinary capillary-rise experiment. Clearly, a gain in sensitiveness is at once obtained by using a light liquid in the manometer. But as said above, any convenient pressure gauge may be used—the micro-manometer devised by Threlfall, the Chattock gauge, the differential liquid manometer,[2] a small receptacle closed by a thin metal disk whose motion may be suitably magnified, or in the absence of these a sloping tube attached to a wide vessel and read by a millimetre scale will give satisfactory results.

The cathetometer is not even necessary to measure the amount by which the capillary is immersed in the liquid. If this distance be determined by attaching a needle to the side of the capillary it is only necessary to form and to caliper a magnified image of the capillary and needle using a good photographic lens.

5. The time of the experiment is appreciably shortened. The accurate determination of a surface tension by the ordinary method is a tedious

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[1] Harkins and Brown, *l.c.*, p. 504.

[2] For a description of this simple and interesting instrument, see Barton, "Introduction to the Mechanics of Fluids" (Longmans), p. 193.

process, and not one to be adventured upon light-heartedly. In our own case we found that, density determinations apart, an experiment involving 32 separate readings of the cathetometer, could be completed in about $1\frac{1}{2}$ hours. (We usually made 8 determinations of the pressure, and 8 of the distance between the needle-point and the end of the capillary.) With a "naked-eye" manometer, this time could be greatly cut down.

We now pass on to consider the experimental details; a diagrammatic sketch of the apparatus is shown below in Fig. 1:—

The pressure required to force the liquid to the end of the capillary is produced by gently raising or lowering the bottle F by means of a rack and pinion, and the corresponding pressure is read off on the manometer C which contains a paraffin of specific gravity 0·856 at 15°. The manometer was read by means of a cathetometer, reading to about $\frac{1}{5000}$th of an inch. The capillary tube was cleaned by means of sulphuric acid and bichromate, distilled water, and alcohol, and was dried by blowing through it heated and filtered air. The tube was then fused on to a wider tube just below the stopcock D. (It may here be recorded that the whole of the apparatus was in one piece—all connections being fused together, and no rubber joints admitted at any point of the apparatus. After any one determination the capillary was cut off, cleaned, and refused into position.)

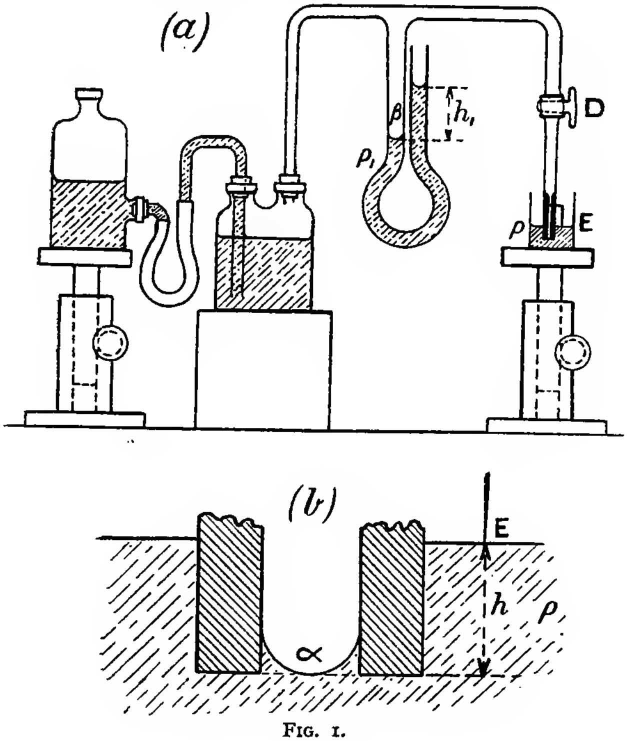

Fig. 1.

The vessel containing the liquid under examination was placed on a movable table and was raised until the surface of the liquid just came into contact with a pointed index E which had been previously firmly fastened to the capillary at a distance h from the end of the tube. This adjustment could be made with great exactness by watching the image of the index point in the liquid surface. By gently raising the bottle F the surface of the liquid in the tube was forced down until the lowest point of the capillary surface, as judged by the eye looking through a low power microscope, was just on a level with the bottom of the capillary tube. The exactness, or rather the *consistency* with which this adjustment may be made is shown by the experimental figures given later. The presence or absence of a constant error in the adjustment was roughly tested by taking readings after adjusting the pressure so that (1) the meniscus just disappeared within the tube, and (2) the meniscus just protruded from the tube; the mean of these pressure readings agreed quite satisfactorily with the "crucial" pressure.

The diameter of the capillary tube was determined by taking the mean of 40 readings (four sets at orientations increasing by 45°). The readings were taken first on the cathetometer used for reading the pressure gauge, and then on a fine dividing engine made by the Cambridge Scientific Instrument Company.[1] The two determinations agreed quite satisfactorily.

The theory of the method is developed as follows:

With the notation of Fig. 1 the pressure at a point α in the air just outside the capillary surface is given by

$$p_\alpha = \mathrm{P} + g\rho h + \frac{2\mathrm{T}}{\mathrm{R}},$$

where P is the atmospheric pressure, T the surface tension, and R the *radius of curvature* at the vertex of the meniscus. But

$$p_\alpha = p_\beta \text{ and } p_\beta = \mathrm{P} + g\rho_1 h_1$$

giving

$$\frac{2\mathrm{T}}{\mathrm{R}} = g(\rho_1 h_1 - \rho h) \quad . \quad . \quad . \quad . \quad (\mathrm{ii})$$

Now writing $a^2 \equiv \frac{\mathrm{T}}{g\rho}$, we know that the height to which such a liquid will rise in a capillary of radius r is, for a liquid of zero contact angle

$$2a^2 = rh_2\left(1 + \frac{1}{3}\frac{r}{h_2} - 0{\cdot}1288\frac{r^2}{h_2^2}\right) \quad . \quad . \quad . \quad (\mathrm{iii})$$

But we have, accurately

$$2a^2 = \mathrm{R}h_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (\mathrm{iv})$$

and therefore comparing (iii) and (iv)

$$\mathrm{R} = r\left(1 + \frac{1}{3}\frac{r}{h_2} - 0{\cdot}1288\frac{r^2}{h_2^2}\right) \quad . \quad . \quad (\mathrm{v})$$

We have from (iii) to a first approximation

$$h_2 = \frac{2a^2}{r},$$

and to a second approximation

$$h_2 = \frac{2a^2 - \frac{1}{3}r^2}{r}$$

or

$$\frac{1}{h_2} = \frac{}{2a^2}\left(1 + \frac{r^2}{6a^2}\right).$$

---

[1] With cathetometer, $d = 0{\cdot}0663$ cm. With dividing engine $d = 0{\cdot}06634$ cm.

Substituting the exacter value in the second term on the R.H.S. of (v) and the more approximate value in the third term we obtain, after a little reduction

$$R = r\left(1 + \frac{r^2}{6a^2} - 0{\cdot}0044\frac{r^4}{a^4}\right),$$

or, quite accurately enough for our purpose

$$R = r\left(1 + \frac{r^2}{6a^2}\right) \quad . \quad . \quad . \quad . \quad . \quad \text{(vi)}$$

Substituting this value of r in equation (ii), expanding and neglecting terms of order higher than $\frac{r^2}{a^2}$, we have finally

$$T = g\frac{r}{2}(\rho_1 h_1 - \rho h) + g\frac{\rho r^2}{6} \quad . \quad . \quad \text{(vii)}$$

as the working equation from which to calculate the surface tension.

The cathetometer used by us was constructed to read in inches. In our case, therefore, equation (vii) takes the form

$$T = gr \times 1{\cdot}27(\rho_1 h_1 - \rho h) + \frac{g\rho r^2}{6}$$

$$= A(\rho_1 h_1 - \rho h) + \frac{g\rho r^2}{6} \quad . \quad . \quad . \quad . \quad \text{(viii)}$$

where densities are measured in $\frac{\text{gm.}}{\text{c.c.}}$, r is measured in *cm.*, and h_1 and h in *inches*.

With one of our tubes, $r = 0{\cdot}03317$ cm., and consequently

$$\log A = 1{\cdot}6162.$$

The table immediately following gives the figures obtained in a determination of the surface tension of benzene.

TABLE II.—(BENZENE).

$\theta = 15{\cdot}5°$ C. $\rho_1 = 0{\cdot}8555$. $\rho = 0{\cdot}8837$. $\log A = 1{\cdot}6162$.

Manometer Readings.			Readings for Immersion of Tube.		
Open Limb.	Closed Limb.	Difference = h_1.	Needle Point.	End of Tube.	Difference = h.
ins.	ins.	ins.	ins.	ins.	ins.
7·658	6·739	0·919	2·266	2·181	0·085
7·657	6·738	0·919	2·267	2·181	0·086
7·658	6·736	0·922	2·268	2·181	0·087
7·658	6·738	0·920	2·269	2·183	0·086
7·658	6·736	0·922	2·268	2·180	0·088
7·658	6·738	0·920	2·258	2·173	0·085
7·659	6·736	0·923	2·258	2·170	0·088
7·659	6·737	0·922	2·257	2·171	0·086
	Mean h_1 =	0·921		Mean h =	0·0864

Hence $\rho_1 h_1 - \rho h = 0{\cdot}7882 - 0{\cdot}0763 = 0{\cdot}7119$.

And from (viii)

$$T_{15\cdot5} = A \times 0{\cdot}7119 + 0{\cdot}16 = 29{\cdot}58 \text{ dyne-cm}^{-1}$$

The relation between surface tension and temperature in the case of benzene is given by

$$T_\theta = T_o (1 - b\theta)^n$$
$$= T_o (1 - nb\theta)$$

for small variations in the temperature, where we may take $n = 1{\cdot}21$,

TABLE III.—(Toluene).

$\theta = 15{\cdot}0°$ C. $\rho_1 = 0{\cdot}8559$. $\rho = 0{\cdot}8715$. Log A = $\bar{1}{\cdot}6162$.

Manometer Readings.			Readings for Immersion of Tube.		
Open Limb.	Closed Limb.	Difference = h_1.	Needle Point.	End of Tube.	Difference ≐ h.
ins.	ins.	ins.	ins.	ins.	ins.
8·432	7·561	0·871	2·636	2·595	0·041
8·430	7·562	0·868	2·636	2·594	0·042
8·430	7·563	0·867	2·634	2·596	0·038
8·430	7·564	0·866	2·635	2·595	0·040
8·430	7·565	0·865	2·637	2·597	0·040
8·428	7·566	0·862	2·635	2·595	0·040
8·429	7·567	0·862	2·636	2·597	0·039
8·443	7·579	0·864	2·636	2·594	0·042
	Mean h_1 =	0·8656		Mean h =	0·0402

$$\rho_1 h_1 - \rho h = 0{\cdot}7400 - 0{\cdot}0350 = 0{\cdot}7050.$$

$$T_{15} = A \times 0{\cdot}7050 + 0{\cdot}16 = 29{\cdot}13 + 0{\cdot}16 = 29{\cdot}29 \text{ dyne-cm.}^{-1}.$$

$b = \frac{1}{288}$, and consequently $nb = 0{\cdot}00420$. Hence, we may write, very approximately

$$T_{15} = T_\theta\{1 - nb(15 - \theta)\} \quad . \quad . \quad . \quad . \quad \text{(ix)}$$

giving a change in the surface tension of about 0·14 dynes per cm. per degree.

From the above experiment, we have, with this value of the temperature coefficient

$$T_{15} = 29{\cdot}65 \text{ dyne-cm.}^{-1}.$$

In Table III. above is given a similar set of readings obtained with toluene.

There is no need to give details of all the readings for the remaining experiments; Table IV. on page 390 gives a conspectus of the results obtained.

The production of authoritative figures for the surface tensions of these compounds forms no essential part of this paper; our main object is to show that the very simple modification proposed removes the chief technical difficulties that beset the capillary-rise method, and that the method does effect this object is almost *a priori* evident. But the discussion of one or two points connected with the above figures will, we think, be of use.

Our experience of benzene has convinced us that this liquid is, for a standard liquid, more than a little treacherous. The six values for T_{15} given above represent but a small fraction of our experimental figures, which, however, group themselves into two classes—one set giving a value of T_{15} of about $29{\cdot}6\ \frac{\text{dynes}}{\text{cm.}}$, the other about $29{\cdot}9\ \frac{\text{dynes}}{\text{cm.}}$. This latter

TABLE IV.

θ.	ρ_1.	h_1.	ρ.	h.	T_θ.	T_{15}.
BENZENE.						
14·4°	0·8551	0·9257	0·8832	0·0900	29·59	29·73
16·1°	0·8562	0·8841	0·8850	0·0357	30·13	30·05
15·5°	0·8555	0·9210	0·8837	0·0864	29·58	29·65
16·0°	0·8552	0·8903	0·8830	0·0590	29·46	29·60
14·8°	0·8559	0·9024	0·8843	0·0530	29·98	29·95
11·0°	0·8585	1·0932	0·8885	0·0488	30·49	* 29·93
TOLUENE.						
15·0°	0·8559	0·8656	0·8715	0·0402	29·29	29·29
16·0°	0·8552	0·8706	0·8704	0·0524	29·05	29·17
METHYL PROPIONATE.						
15·5°	0·8555	0·7699	0·922	0·0342	26·09	—
11·1°	0·8584	1·0280	0·926	0·1241	* 26·31	—

(The starred results were obtained using a new tube for which $r = 0·02724$ cm., and therefore log A = 1·5307.)

figure is the value which we generally obtained after performing all the usual rites associated with the purification of benzene. It was only when, in addition, we made several fractional crystallisations of the specimen, and then *immediately* determined the surface tension, that the lower figures were obtained. On allowing the benzene to stand for a few days its surface tension reverted to the higher value.

Whatever be the apparatus employed for the determination of surface tensions, it is clearly advantageous to have at hand a standard liquid which can be used to test the apparatus. We ourselves feel that benzene is far from being the ideal liquid; for it in several respects falls short of such a standard, which should

(i) be easily prepared;
(ii) be easily purified;
(iii) be non-hygroscopic;
(iv) not be liable (like water) to surface contamination;
(v) not attack glass.

In Table IV. above, the first, third, and fifth results were in each case taken immediately after three fractional crystallisations of different specimens of purified benzene. The mean of these gives

$$T_{15} = 29·66 \frac{\text{dynes}}{\text{cm.}}.$$

In Table V. on following page are given a few of the results obtained by other experimenters.

It seems then that, with the exception of Renard and Guye's value,[1] the value we have obtained is in very close agreement with the values given by the ordinary technique of the capillary rise method. The latest and most careful experiments are those of Harkins and Brown, and of Richards and Coombs, and our mean value agrees with theirs to about 1 part in 500.

These experiments were carried out in the Physical Laboratories of the Manchester College of Technology, and it is our pleasant duty to thank Professor Gee or the assistance which he has given us, and for the facilities which he has placed at our disposal.

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[1] Ramsay and Aston's value is for the surface tension of benzene in contact with its saturated vapour.

TABLE V.

Experimenter.	Method.	T_{15}.
Volkmann . .	Capillary rise .	29·51
Harkins and Brown .	,, ,, .	29·59
Ramsay and Aston .	,, ,, .	28·68
Renard and Guye .	,, ,, .	28·45
Richards and Coomb.	,, ,, .	29·61
Ferguson . . .	Jaeger's method	29·65
Feustel . . .	,, ,,	30·9

College of Technology,
Manchester.

December, 1920.

Dr. F. C. Thompson, D.Met., B.Sc., contributed to the discussion the following note on **"The Interfacial Tension Between Carbide of Iron (Fe_3C) and Iron".**

The probability that surface energy plays an important rôle in determining the mechanical properties of metals has received increasing attention since 1915, when a paper was read before the Faraday Society[1] in which the suggestion was made that such phenomena at the crystalline boundaries might be a dominating factor in determining the elastic limit of the metal.

No attempt, however, appears to have been made to determine in the case of solid metals the magnitude of such effects. It is possible in certain cases, however, to utilise the method of Ostwald and Hulett which has already yielded interesting results in the case of the solid sulphates of calcium and barium. The measurement of the interfacial tension between Fe_3C and iron was made by determining from the electrical resistance of the samples of the same steel hardened together, but tempered at 500° C. and 650° C. respectively, the influence of the size of the carbide globules on the solubility of cementite in iron.

The steel used had the following analysis :—

C per cent.	Si per cent.	Mn per cent.	S per cent.	P per cent.
0·69	0·144	0·68	0·049	0·019

and was received in the form of wire about $\frac{1}{10}$th of an inch in diameter. A length of 27 inches was heated to 780° C., quenched in water, and then tempered at 500° C. As a result of this treatment the material possessed a structure consisting of very fine globules of Fe_3C embedded in a matrix of more or less carbon free iron, *i.e.* sorbite. A second piece was reheated to 650° C. for several hours and cooled in air, and a structure of a similar type to the previous one but with much coarser globules was induced.

After having been well cleaned with emery cloth to remove scale and any decarburised surface and then carefully straightened the specific resistance of each material was measured on a Kelvin double-bridge apparatus which has been checked against a standard resistance of 0·01 ohm. The fall of potential along a length of 50 cms. was measured, the exact point of balance being obtained by noting the deflections produced by contacts very slightly displaced on each side of the point. The diameter of each wire was very carefully measured at five points by a micrometer sensitive to 0·00001 ins.

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[1] *Trans. Faraday Soc.*, 1915, xi., 104.

The values of the specific resistances at 10° C. are:—

(*a*) Quenched and tempered at 500° C. 17·873 microhms per cm. cube.
(*b*) Annealed at 650° C. . . . 16·732 ,, ,, ,, ,,

Benedicks has shown[1] that the presence of 1 per cent. of carbon in solution in iron raises the resistivity by 26·8 microhms per cm. cube. If the difference in the resistivities in the case examined is due to the increased solubility of the carbide due to the fineness of the division of the globules, this difference of solubility must be 0·042 per cent. carbon.

It should be remembered that this represents the increased solubility at 500° C. at which temperature the structure was produced. It is difficult to say exactly what is the normal solubility of carbon in iron at this temperature, but it is unlikely that it will exceed 0·02 per cent., and by using this value as a basis for the calculations a minimum value of the interfacial tension will be obtained.

The measurement of the size of the particles was a matter of difficulty and is certainly the most inexact portion of the work. The structure magnified 1500 diameters, a 2 mm. objective of N.A. 1·35 being used, was projected on to a glass screen and the diameter of particles measured. The result for the smaller globules was of the order of 0·00001 cms.

The formula used[2] was:—

$$R\theta \log_e \frac{\lambda'}{\lambda} = \frac{2\sigma}{\rho a}, \text{ where}$$

λ' is the solubility of carbon in iron where the globules have a radius a,
λ is the solubility in the case of large masses,
σ is the interfacial tension of Fe_3C against iron, and
ρ is the density of cementite.

In the case of the slightly nickeliferous meteoric mineral Cohenite ρ is 7·24.

Thus:—

$$8{\cdot}5 \times 10^{-4} \times 773 \times 2{\cdot}3 \log_{10} \frac{0{\cdot}062}{0{\cdot}02} = \frac{2\sigma}{7{\cdot}24 \times 10^{-6} \times 5}$$

Where

$$\sigma = 1350 \text{ dynes per cm.}$$

This result is of the same order as the surface tensions of solid barium and calcium sulphates.

DISCUSSION.

The Chairman, I am sure we have listened with great interest to the papers which Dr. Ferguson has read and in which he has covered the whole subject. I have been interested myself for a long time in this subject, chiefly from the theoretical point of view, but also in part from the experimental side. I have had considerable experience in attempts to measure the surface tension of mercury by means of the drop method, but, of course, taking the precaution to use very large drops, a precaution which, we have been told, is so necessary for the application of any simplified formula. The method that I actually adopted was somewhat different from anything that has been described to-night. It consisted in photographing a sessile drop and by means of graphical methods determining the correction to the elementary formula. I should like at this point to ask Dr. Ferguson what special precautions he would take in connection with the illumination. That is really an exceedingly important point. If you merely take chance illumination, the contour of the drop may be made almost anything you please, and I think it would be of great interest to those who are experimenting on drops, if Dr. Ferguson could give us some details as to the actual illumination that he recommends.

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[1] Doctorate Thesis Upsala.

[2] "Surface Tension," Churchill, 2nd edition, p. 27.

The particular point in connection with the second paper—that is, the paper describing this new method—which interests me is that it seems to me that it provides a much more satisfactory way of determining the surface tension of a solution than the ordinary capillary tube method does, because, if you have a solution rising up a narrow capillary tube, you have very great uncertainty as to what the concentration of the liquid will be in the capillary tube near the surface, which is the place which is all-important in connection with measurement. On account of adsorption along the wall of the capillary, the concentration near the surface may be very considerably changed. But if you force the liquid down until it comes to the end of the capillary, there is very much more chance of diffusion taking place and of the concentration at the depressed surface becoming thereby the same as that in the body of the liquid.

There is, in general I suppose, more uncertainty in the measurements for solutions than there is in measurements for pure liquids, and Dr. Ferguson has shown you the great variation that different experimentalists have obtained even in the latter case. He did not quote Quincke's value of 81, which is still given in a great many text books as the value of the surface tension for water, but I may tell you that Quincke has never withdrawn that number. He still thinks that the value 81 is the better value, instead of those in the neighbourhood of 73 or 74, and that the reason why it is so high is that he obtained specially pure water. Of course, the very slightest contamination reduces the surface tension of water and it is rather difficult to disprove a statement like that; moreover, Quincke was an exceedingly careful experimentalist. Yet, I think, the balance of evidence at the present time is against him.

The subject of surface tension is important, not only from the theoretical point of view, but on account of its practical application. I have only to recall to technologists the process of the flotation of ores, in connection with which a great deal of work has been done. And in that process, or in trying to explain the process rather, it is exceedingly important to measure the surface tension between a liquid (which has been slightly modified by adding another) and a solid particle suspended in it. So that it is the problem of the surface tension at the surface of separation between a solid and a liquid that is of greater practical importance than any other. This is, however, just where the greatest difficulty arises in regard to experimental determinations.

I will now give briefly a theorem that occurred to me a few years ago, and which I have never published because I wanted to collect some data in connection with it before publication. I have not yet had an opportunity of doing this. But I think it would be useful to mention the theorem now.

When a solid is dissolved in a solvent the surface tension against the air (or vapour) surface sometimes increases and sometimes decreases. There will also be a change in the interfacial tension between the solution and the solid (*i.e.* the walls of the vessel or solid suspensoids, etc.). This theorem connects the two changes.

Let the meeting-point of a solid, solution, and gas be as shown. The surface tensions at this point are connected mechanically by the relation

$$T_{13} = T_{23} + T_{12} \cos \alpha$$

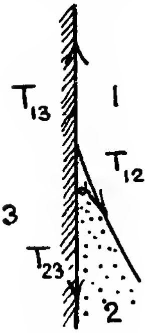
where α is the angle of contact. Let now the concentration c of the liquid be increased; then, it follows that

$$0 = \frac{\partial T_{23}}{\partial c} + \frac{\partial}{\partial c}(T_{12} \cos \alpha).$$

Let us keep to the cases for which α is *practically* zero ; then practically

$$\frac{\partial T_{23}}{\partial c} + \frac{\partial T_{12}}{\partial c} = 0 ;$$

or in words :—



The surface tensions of a solution against a gas and a solid change *in opposite senses* with a change in concentrations provided that the angle of contact is nearly zero.

This is an exceedingly simple, and at the same time, important result in connection with the application of Gibbs' adsorption formula.

I do not wish to take up all your time. There are two other points I will just mention. One is in connection with Mr. Ferguson's power formula for the dependence of surface tension upon temperature $T = T_0(1 - bt)^n$, which he takes as replacing Ramsay's linear law. The drawback of the latter law was that it does not make T zero at the critical temperature.

Now, Einstein pointed out in 1901[1] that it is the total energy which is much more important than the surface tension, the connection between them being

$$U = T - \theta\frac{\partial T}{\partial \theta}$$

where U is the total energy, T the surface tension, and θ the absolute temperature. Whittaker in 1908[2] comes to the same conclusion, and states that there is no reason for supposing that U vanishes before the critical temperature is reached. He further finds that U for a liquid in contact with its own vapour at any temperature is proportional to the product of the internal latent heat and the absolute temperature.

The bearing of this upon Mr. Ferguson's equation is that this equation makes T vanish at the critical point, whereas with Whittaker it is U that should vanish. It seems to me exceedingly probable, from every point of view, that *both* of them vanish there. It is not easy to conceive any difference for one more than for the other. An examination of the data given by Whittaker shows that this is likely. In other words U changes very fast (infinitely so) in the neighbourhood of the critical point while $\frac{\partial T}{\partial \theta}$ becomes zero; so that at the critical point U = T. This is quite in agreement with Mr. Ferguson's equation for according to it

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[1] *Ann. d. Phys.*, 4, p. 513.

[2] *Proc. Roy. Soc. A.*, 81, 21.

$$\frac{\partial T}{\partial \theta} = \text{const. } (1 - bt)^{n-1}$$

if h is the reciprocal of the critical temperature as I take it to be.

Dr. A. M. Williams: I have listened with very great pleasure to Dr. Ferguson. I am rather sorry, personally, that he did not give us a longer discussion on the drop method, which he does not appear to like very much. My chief interest in surface tension is not to measure it, though I must say I admire very much the photographs which Dr. Ferguson has shown us, but to get at the results for the sake of theoretical calculations. I am rather interested at the present time in the examination of surfaces which is going on industriously in America and in Britain. I particularly refer to the investigation which is due, more or less, to two men in America (Langmuir and Harkins), who have taken up the idea (advanced, I think, by Haber) that a surface is not the simple thing we thought it. These men have been looking carefully into what goes on in the surface, and they are bringing forward evidence to show that the surface differs from the mass of the liquid and from the mass of the vapour, and resembles to some extent a crystalline solid. They came to the conclusion, then, that the liquids examined were behaving in a special manner, and they concluded that you might say that a molecule containing a particular group was orienting itself so that that group came to the surface or was buried in the surface. They were measuring the surface tension associated with that group. Such liquids they called polar. . . .

This is borne out by measurements made by Barger when working on adsorption. He was interested in the staining of starch by iodine which turns to blue. He examined first of all a glucoside, and he knew there was associated with this a special group, so he took the trouble of preparing a whole sequence of substances (containing this group), got them in a colloidal state, and then they one and all were coloured blue with the iodine. This suggests, of course, that you have in the colloid surface an orientation of the group in question. Langmuir assumes that on a crystalline surface, the crystal forces come into play and molecules are thereby attracted to the surface. I am very much intrigued with this theory myself.

One thing I was rather struck by in the paper was that Dr. Ferguson appeared to measure surface tension of liquids chiefly against air, not against their own vapour. This applies particularly to his pressure method. A rather curious thing was the behaviour of the benzene. He found that he got benzene, after standing, giving a higher surface tension than benzene (freshly prepared). Professor Lapworth suggests this is due to adsorption of water vapour, but if so, it must be *negative* adsorption.

To come to Professor Porter's little theorem which he put on the board, I disagree with him when he excludes the variation of the first term. I do not think the variation of the first term with the concentration is great; but I do not think it is non-existent.

Dr. R. S. Willows: I agree with Dr. Williams on the importance of accuracy in these measurements from the point of view of distinguishing these modern theories of surface tension for one thing, and also for distinguishing theories of emulsification. It is about time that some reasonable theory was formed as to when and why you get certain things happening in emulsification, and I think the lack of reasonably accurate measurements is a great difficulty in the way of forming any reasonable theory.

Dr. Thompson has shown us how important it is to get a value of surface tension in his subject of metallography. There are some questions I would like to ask Dr. Ferguson. If we are going to use Dr. Ferguson's method for technical work it is going to be rather serious. What we want is some method for technical work that will produce the same simplication of measurement as we get in the case of measurements of refractive index by a refractometer instead of a spectrometer.

How are some of Jaeger's methods affected by viscosity? For example, in my work, we are constantly dealing with liquids that are very viscous. What, as a practical method, would Dr. Ferguson suggest could be used for such liquids as these? I am asking simply because we want a method that can be used rapidly to estimate surface tensions. If we could get any method of measuring surface tensions quickly it would be a very great advantage.

The method in Dr. Ferguson's second paper is an exceedingly good one. It has, however, been used before, although not published before. Dr. Searle gave this method to students to use in the Cavendish Laboratory. I am afraid Dr. Ferguson's method of photographing the drop will be rather a long one, but probably it is a great deal more accurate than the drop one.

Professor A. Lapworth said that he was especially interested in the time variation of the superficial tension of benzene. This change required further investigation.

Professor W. W. Haldane Gee referred to the work of Quincke, who was still working at the age of eighty-seven on the subject of surface tension. Recently he had given a new theory of the constitution of glass depending on surface tension. Professor Gee worked for a short period in Quincke's laboratory at Heidelberg, and he remembered that Quincke insisted on many precautions in obtaining the value of the superficial tension of water by the capillary tube method, especially in the avoidance of contamination by dust.

The discussion was continued in London at a meeting held on Monday, May 9, 1921, in the Rooms of the Chemical Society, Burlington House, **Professor Alfred W. Porter, F.R.S.**, President, in the Chair.

The Chairman said it occurred to him, as he had said at Manchester, that Dr. Ferguson's method would be an exceedingly good one in the case of solutions, compared with the ordinary method of the capillary tube in which the solution had to pass into a glass tube with walls that were, perhaps, not over clean, although they might have been considered to be clean. It was a great advantage in Dr. Ferguson's method that the solution remained at the end of the tube, and if there had been any collection of dirt there or any adsorption on the walls of the tube, there was an easy means of getting fresh liquid to the end by merely bubbling air through. If there was any disturbance for the moment it would very quickly adjust itself, so that there would be practically the same concentration for the liquid at the end as in the main body of the liquid. The method, therefore, ought to be exceedingly useful in such cases, and Mr. Sutherland was actually making experiments in that direction. There were many other things to be said about the papers; he would content himself at the moment with congratulating Dr. Ferguson on his very simple modification of already existing methods.

Mr. S. Sugden referred to the suggestion in Dr. Ferguson's paper as to the difficulty of getting consistent results with benzene. It was not always appreciated, he said, that benzene is a rather hygroscopic substance, and although to make benzene free from water was not difficult at all, it was very difficult to keep it free from water. He thought that some of the higher values, such as 29·99 and figures of that order mentioned in the paper, might have been due to the presence of traces of water. The apparatus itself might allow traces of moisture to be adsorbed at the exposed surface of the liquid. A second point was the size of the surface tested. Richards had shown that in many cases the comparison surfaces used were not large enough and that might have been the case in the present instance. At all events, the size of the surface would receive consideration. It was important to have it perfectly flat at the centre, or to apply a suitable correction.

Mr. E. Hatschek said he would like to see the method adapted to interfacial tensions, because that was the greatest bugbear there was at the present time. It was almost impossible with the ordinary capillary method, whilst the ordinary drop method was pretty bad, even if carried out carefully, and it was never carried out carefully. Therefore, in colloidal chemistry there was great interest in a good method for measuring interfacial tensions and the adaptation of Dr. Ferguson's method seemed fairly obvious.

Mr. G. A. Sutherland, speaking with regard to the size of vessel necessary to eliminate the effect of curvature, said he had been thinking about that matter. The question had been worked out theoretically by the late Lord Rayleigh and there was a paper in the current number of the *Journal of the American Chemical Society* by Richards and Coombs describing work in which they verified experimentally the values that Lord Rayleigh found. He believed Rayleigh found that there should be nearly 5 cm. of diameter in a cylindrical vessel in order to ensure that the surface was flat at the centre. The case in which a tube dipped into the vessel had not been worked out. With regard to the ellipticity of the bore, that, too, was dealt with in this paper, and it was shown that even as much as 2 per cent. difference in the two diameters made a difference of only $\frac{1}{100}$th per cent. in the value of the surface tension. It was easy enough to find a tube, with a little searching, which had no more variation than that. With regard to the higher values that Dr. Ferguson sometimes found for benzine, it was mentioned in the paper that these higher results were obtained when he did not carry out the determination immediately after purification of the liquid. When he carried out the determination at once he got the lower values. Nevertheless, he was sure Dr. Ferguson would be interested in the suggestion that had been made.

Dr. Ferguson (*in reply, partly communicated*): The correct illumination of a drop or bubble is, as the President has said, of the first importance. If due care be taken, there is little danger to be feared on this head. In photographing large sessile drops, or large air bubbles, a cylindrical lens may be used. This gives a long horizontal beam which is limited by a number of narrow horizontally placed rectangular apertures. A very small upward or downward tilt of the beam produces a notable blurring of the outline, so that it is relatively easy to determine the proper conditions of illumination. I think that a careful inspection of the actual photographs will show that it is the "true" contour of the bubble or drop which is exhibited.

Professor Porter makes a valuable contribution to the discussion in his remark concerning the avoidance of adsorption by the use of the method described in the second paper; I hope that Mr. Sutherland will shortly be able to give us some figures for the surface tensions of solutions which can be compared with those obtained by other methods.

I am sorry that I was unable to satisfy Dr. Williams' desire to hear more of the drop method. On the one hand, time pressed, and on the other hand I find it difficult, in discussing this much used (and misused) method to employ language which is at once accurate and suited to the austere atmosphere of scientific debate. If there is one point which, more than any other, I could wish to be made quite clear by this discussion, it is the urgent need for measurements of interfacial tensions by independent methods, thus furnishing figures by which we could check the values given by the drop method. I do not wish my words to be taken at more than their face value—the drop method, properly used, may or may not give consistent and accurate values for an interfacial tension. But what *is* abundantly clear is that the method, as usually applied in technical research, gives figures of more than doubtful value. I am glad to find Mr. Hatschek in agreement with me on this point. As he says, the adaptation of the method I have described is fairly obvious, and it is one of the principal functions of the first paper to describe other promising methods of attack upon this difficult problem. I hope in the future to give some results obtained by the use of methods there outlined.

Preliminary observations are usually tedious, and the technique of the photographic methods is not yet so simple as it might be. But, assuming that the best method for measuring interfacial tensions is a photographic one, I do not apprehend any special difficulty in the technique. A properly designed apparatus, permanently set up, so that the illumination is in perfect adjustment and the exact setting of the drop or bubble is a mechanical matter, will enable one to take a photograph with very little loss of time; and the measurement of the outline, and the resulting computations, need involve no more time or trouble than is associated with the accurate practice of any capillary-tube method.

Viscosity is undoubtedly troublesome in the practice of Jaeger's, or of any other method which is not absolutely statical. My own experience has been that the Jaeger method works very well with liquids rather less viscous than is glycerine at ordinary temperatures; with glycerine (and, *a fortiori* with more viscous liquids), the method is troublesome. With such liquids an absolutely statical method must be used, and time is necessary for the liquid to attain its equilibrium position. I am afraid that I do not know any general method by which a viscous liquid may be hurried into this position. If a liquid is viscous, it *is* viscous, and, as Johnson remarked in another connection "there's an end on't". But, for liquid-air tensions specially, I would suggest one of the balance methods classified above as likely to be least extravagant of time.

The correction due for the size of the containing vessel has been worked out, with characteristic clearness and precision, by the late Lord Rayleigh. Since the publication of this paper, no excuse exists for an experimenter who, without making any correction, uses an external surface smaller in area than theory demands, and I have been fully alive to the importance of this point. To whatever cause be due the variations in the surface tension of benzene, they are certainly not due to this, and as Professor Lapworth suggests, the change merits further investigation. The remarks made in the discussion serve to emphasise still more strongly the unsuitability of benzene for use as a standard liquid.

THE ELECTROLYTIC RECOVERY OF ZINC.

By Samuel Field, A.R.C.Sc. (Lond.).

(*A Paper read before* The Faraday Society, *Tuesday, March* 22, 1921,
Professor Alfred W. Porter, F.R.S., President, *in the Chair.*

Abstract.

The electrolytic recovery of zinc is advocated as an economic proposition in Great Britain. The British spelter industry is at present very depressed and there is room for an enormous increase in the output of zinc. Home ores should, if possible, be used. Abundant supplies of low grade and complex ores are available. They are not amenable to distillation but respond readily to alternative electrolytic treatment. Processes have been worked out to effect economic recovery. Sulphide ores are calcined to oxide and a predetermined proportion of sulphate. The calcine is leached with acid zinc sulphate liquors (3 per cent. Zn + 10·5 per cent. H_2SO_4) from the electrolytic cells. Special treatment avoids gel formation, and admits of high extraction and easy filtration. The lead-silver residues go to the blast furnace, *via* sintering, for the recovery of argentiferous lead.

The zinc sulphate solution is much too impure for efficient deposition. High purification is a *sine qua non* for subsequent economic deposition. The methods worked out are given in some detail and comprise the use of such oxidising agents as air, ozone, lead and manganese dioxides for the removal of Fe, As, Sb, and Co. Zinc dust in a slightly acidified solution readily removes Cu, Cd, and Ni, greater speed of elimination being obtained with the concomitant elimination of Co by the prior addition of about ·005 to ·01 per cent. Hg as sulphate. Ni and Co constitute two commonly met and insidious impurities. The purified liquors contain not more than 3 to 5 parts Co and ·2 part Ni per 1,000,000. The pure neutral solution is acidified down to 8 per cent. Zn + 3 per cent. H_2SO_4 and electrolysed between lead anodes, which in the absence of certain impurities are very permanent, and aluminium cathodes. The liquors attain a desirable maximum temperature of up to 40-45° C. and the cells, arranged in cascade, absorb 3·35 volts and give a current efficiency of 90 per cent. This represents about 3200 K.W.H. per ton of zinc cathodes. The outflowing liquor is used cyclically for extraction and acidification.

Subsidiary power is amply covered by 800 K.W.H. per ton. Hence 4000 K.W.H. ($\equiv$ 160 K.W. per ton cathode zinc per day) covers all power. This should be raised from low grade fuel at ·32d. to 35d. per unit. At ·33d., power costs are £5 11s. per ton of cathode zinc.

The cathodes are melted and yield ingots assaying not more than ·02 per cent. Pb, ·02 per cent. Cd, and ·01 per cent. Cu and Fe together, with at least 99·95 per cent. zinc. Purification is simplified if only a 99·92 per cent. product is required.

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I. INTRODUCTION.

Very little has, we believe, appeared in the British technical press, relative to the subject of electrolytic zinc. The problem has, however, claimed considerable attention in other countries and especially in the United States. Yet its possibilities have for a long time been recognised, and the subject claimed attention even as far back as the eighties, at which time, however, electro-metallurgy had not advanced sufficiently to even indicate the lines upon which the problem might ultimately be solved. Electro-metallurgists were then, and indeed for a long time after, mainly concerned with the production of coherent deposits of the metal. When that problem was solved the even more difficult problem of economically obtaining from natural resources of zinc, solutions adapted to large scale successful deposition, arose. Now all this has been changed and from the point of view of the development of the country's resources the problem rather is that of the utilisation of home ores in the development of a home industry bringing with it a greater measure of independence of remote resources of metal and ore. Indicative of the importance of the subject it will be within recollection that during the war the price of spelter soared to £115 per ton from a pre-war value of £21 to £23 per ton, and that recently three of the largest spelter works in South Wales representing probably 50 per cent. of the country's capacity have shut down owing to difficulties attaching to lack of suitable ores and high labour costs, believing, presumably and reasonably, that zinc production should be an economic proposition and not a matter of industrial philanthropy. In fact, even labour troubles in Australia have had a direct influence on the important zinc industry in preventing the exportation of zinc concentrates to this country.

The development of a home industry in electrolytic zinc and utilising home resources thus assumes paramount national importance.

A few years ago excellent papers constituting a résumé of the zinc industry were compiled by Messrs. J. C. Moulden and E. A. Smith, that by the latter being subsequently expanded into his now well-known work "The Zinc Industry". But in neither of these or in other contributions to the literature of zinc metallurgy has adequate reference been made to the electrolytic phase of the subject. We feel we are safe in claiming that, with the exception of an article by Capt. S. C. Bullock in "Metal Industry" of February, 1920, this is the first definite proposal which has been made, based on a long and careful series of tests on both laboratory and works scale, for the establishment of a British industry in electrolytic zinc.

II. British Zinc Industry.

Great Britain is said to be the largest non-ferrous metal consuming country in the world. In these metals it is, at the same time, very far from self-supporting. Its great engineering industry is dependent upon these metals not much less than on iron and steel.

The position of the metallurgy of zinc in this country prior to the war was typical of the deplorable condition of non-ferrous metallurgy generally. During many years Great Britain has been losing its premier position as a metallurgical centre, and the growth of metal consuming industries and their demand for metals had far out-distanced the country's production. Thus, in the case of zinc, the position in 1913 was roughly as follows:—

Annual consumption	220,000	tons
Annual production	60,000	„
Annual importation	160,000	„

This importation was made up thus:—

From Germany	64,000	„
From Belgium	53,000	„
From Holland	10,000	„
From U.S.A.	5,000	„
From other countries	28,000	„
	160,000	„

More recent Board of Trade returns go to show that in this country during the past five years the annual production has been 50,000 tons against a consumption of 180,000 tons. To-day the zinc industry is sorely depressed and an annual output of 20,000 tons is probably the present measure of the industry. Even without counting on any future expansion of the zinc consuming industries beyond pre-war dimensions, there is thus a very large field for the development of zinc metallurgy in this country.

III. Distillation and Electrolytic Processes.

This lagging of the British industry is due mainly to the approaching exhaustion of the supplies of high-grade ores, so indispensable to the long established, though very wasteful, process of smelting known as distillation. The chief disadvantages of distillation are:—

1. It necessitates high-grade ores of which few only are now available in this country, and hence the method must rely on

2. Imported raw materials, with all the possible restrictions of transport and high freightage charges and those always attaching to times of emergencies.

3. It demands highly skilled manual labour, a most important item. There is, further, very little or no reduction in the proportionate labour cost with a larger plant.

4. It yields only a recovery of as low as 70 to 75 per cent. of the metal.

5. The product is impure, ranging only from 98 to 99 per cent., and commercially known as G.O.B. (good ordinary brands).

6. It fails to recover concomitant metal values such as lead, copper, cadmium, silver, etc., while,

7. These metals further act detrimentally to the recovery of the zinc.

8. Very large bodies of low grade zinc ores (untreatable by distillation) abound in many parts of the world and also in this country.

As a result, the distillation process is being abandoned in America, Australia, and Tasmania, and is being replaced by the newer electrolytic process. Distillation is thus destined to give place to the extending electrolytic process, for which the following claims are proved:—

1. It successfully treats low grade zinc and complex ores, that is, zinc ores chemically combined with galena and other minerals.

2. These ores are of lower value per unit of zinc on account of their complexity.

3. It gives a higher recovery than distillation, up to 85 to 90 per cent.

4. It also recovers other metal values, such as copper, cadmium, lead, and silver, which in distillation are worse than valueless and these metals thus become sourcesof additional revenue.

5. In all its stages it is mechanical and demands little or no skilled attention.

6. It yields a very high grade product up to 99·95 to 99·98 per cent.

7. It brings into the sphere of utilisation large bodies of home ores not amenable to distillation.

8. The cost of operation is less than that of distillation.

9. A process has been completely and successfully worked out on a commercial scale for treating all types of complex ores both from British and foreign mines, including Australian concentrates. The experimental work has involved the production and sale of over 120 tons of electrolytic zinc.

10. It thus opens a wide field for the development of a home zinc industry, thus rendering the engineering and other industries of the country much less dependent upon outside resources of ores and labour conditions.

Electrical power is a matter of immediate development, and the consumption for electrolytic zinc is only about one-sixth that for the same weight of aluminium.

The pure product has enhanced properties, and wider fields of utility are continually being opened up in addition to a superiority for all purposes for which G.O.B. spelter is at present employed.

Thus from every point of view, the time is propitious for the establishment of a Home Electrolytic Zinc Industry.

IV. Developments Abroad.

It is not generally recognised that the electrolytic method has commanded considerable attention abroad, and that a number of large plants are in successful operation. The circumstances favouring each of these developments are worthy of consideration and can in no way be construed adversely to a similar development at home until home conditions have been fully explored. It may, in this connection, be called to mind that the Anaconda Copper Company has an electrolytic zinc plant in operation, turning out at the present time up to 150 tons of metal per day. At Trail, B.C., a 75 ton per day plant is in operation. The Judge Mining Company are now turning out daily 9 tons while a number of smaller works are also nearing completion or actually running. In America, at any rate, the industry has passed from its infant days. At Risdon, in Tasmania, a 20 ton a day plant is in commission and extensions up to 100 tons per day are being rapidly pushed forward. While the whole of the difficulties attaching to the British spelter industry have not been so acutely felt in these other countries, the experience of but a few of them has sufficed to lead to the developments mentioned, but in each case the industry is governed by purely local conditions. These developments can only be regarded as a sign of the zinc times and of the larger substitution of the electrolytic for the distillation process. Are we in Great Britain, with all our metallurgical prestige to be content to merely bring up a distant rear? The figures given above should suffice to impress a lesson that we in this country must not be behind in establishing the more modern method of zinc metallurgy. Brief mention may also be made of the electro-thermal methods now being tried out in some countries in which the cost of electric power developed hydraulically is of a very low order. The very high consumption of electrical energy, amounting to about 12,000 kw. hours per ton of metal, at once rules the process out of court as a commercial proposition in this country.

Narrowing down the possibilities of a successful electrolytic zinc industry in this country, it becomes necessary first to consider the relation of the all-important matter of ore supply, in order to guarantee the continuance of the industry even in times of emergency of restriction of imports such as that through which we have recently passed.

V. British Ore Supplies.

The fact of the rapidly decreasing resources of zinc ores in the United Kingdom available for distillation is perhaps best evidenced by the arrangements which were made by the Government for the importation of Australian concentrates. "While the war lasts, a minimum of 100,000 tons annually of concentrates will be treated within the United Kingdom, and the quantity may be increased to 150,000 tons. For ten years after the war Great Britain will take at least 100,000 tons of concentrates annually, and 45,000 tons of spelter produced in Australia will be taken by Great Britain." The rate of importation which at present obtains, makes it difficult to determine in which, if either, of the two periods above mentioned we are now living.

Many, if not most, of our zinc mines have ceased to be profitable when considered from the point of view of distillation. Ore complexity was met, the value rapidly decreased, and now, where mining operations terminated as far as distillation was concerned, the electrolytic process is able to step in. As concrete examples it may be stated that 1,000,000 tons of ore in Cornwall and large bodies of similar ores in Scotland which have been turned down not only from the distiller's point of view but also by some workers in electrolytic, have been prospected and are being rendered available for the electrolytic process which has been worked out partly on these materials. With a choice of suitable materials at home and abroad, preparedness for emergencies will dictate a policy to be adopted in working them.

The success of any electrolytic process, will, however, always need to be judged by its adaptation to local conditions. A simple electrolytic process as used abroad is quite inadequate to the economic treatment of home ores which are notoriously complex and difficult of treatment, and wide variations of operation have thus become necessary and have been worked out and applied with the completest success.

VI. Outline of Process.

In a few words the process may be described as one of calcining sulphide ores to render the zinc soluble in sulphuric acid by which it is extracted as zinc sulphate and which, after purification, is electrolysed with insoluble anodes, zinc being deposited in an easily detachable form and subsequently run down to ingots. While such a process is simple when carried out, as it is in other countries, on the comparatively pure ores there available, any successful electrolytic process must legislate for all possible disturbing impurities and the intricacies of the process are those associated with the elimination of small traces of insidious impurities rather than merely recovering the bulk of the zinc. In simple outline, the process is shown in Fig. 1.

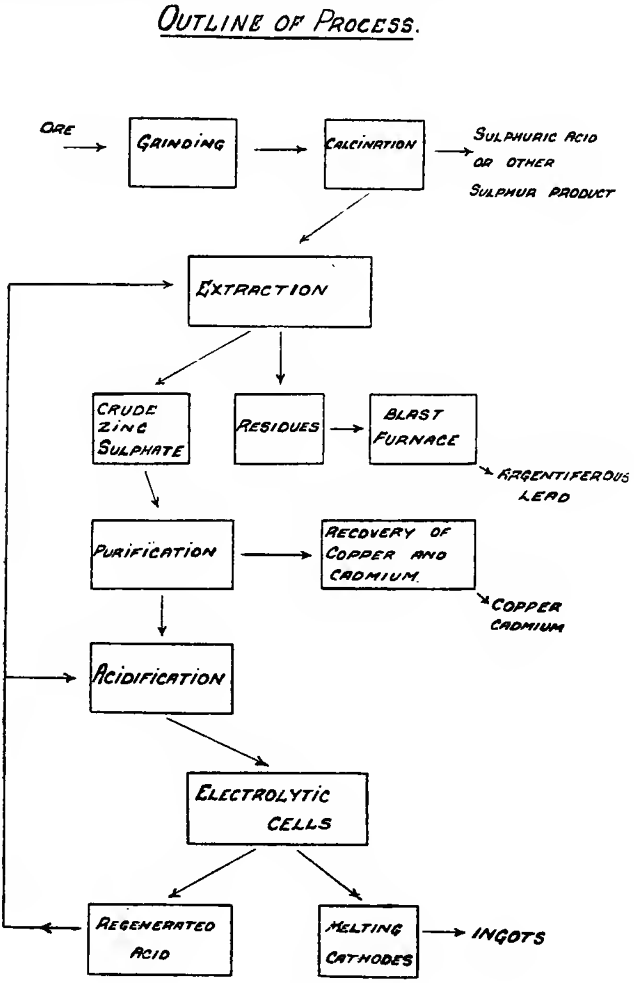

Fig. 1.

(*a*) *Calcination* is conducted under special conditions designed to render the subsequent process of extraction highly efficient.

(*b*) *The extraction* of zinc from the calcined ore by the acid liquor containing about 3 per cent. of zinc and 10·5 per cent. of sulphuric acid from the electrolytic cells is carried on with an efficiency varying from 85 per cent. to 90 per cent. and over, according to the grade of the ore, lower grade ores giving the poorer extractions.

Crude zinc sulphate solutions thus produced may now contain in addition to 10 per cent. of zinc:—

·05	per cent.	of	copper,
·03	,,	,,	cadmium,
·10	,,	,,	manganese,
·05	,,	,,	iron,
·001 to ·01	,,	,,	cobalt,
·001 to ·01	,,	,,	nickel,

together with small amounts of antimony and arsenic. The whole of these impurities, with the exception of manganese, are well recognised by electrolytic zinc experts to be highly detrimental to the further process of zinc deposition. Almost the sole requirement for successful zinc deposition is a pure zinc sulphate solution.

(*c*) *The purification* of the crude liquor is therefore a matter of paramount importance. Methods for the removal of copper, iron, and cadmium have long been used. It has, however, been recognised that cobalt and nickel are two of the most insidious and cumulative impurities—cumulative in the sense that, not being removed by simple processes usually adopted, they accumulate in the liquors with disastrous effects upon subsequent electrolysis. Of nickel, it has been placed on record that "a minute fraction of 1 per cent. in an ore would render that ore untreatable by the electrolytic process, and that the removal of the nickel constitutes a most complex chemical engineering operation".

Special methods therefore for which patents have been granted in this and other countries have been devised to successfully reduce the quantity of nickel which normally occurs in the zinc solutions down to so small a degree as to produce absolutely no detrimental effect on the subsequent process of deposition. The same remark applies also to cobalt, which has proved an insuperable difficulty to many workers in electrolytic zinc.

These recently discovered methods are entirely successful in reducing these impurities and others of the rarer type almost beyond recognition, and beyond the point at which they reduce the efficiency of deposition. In addition, the elimination of each of these impurities is not a matter of separate operations. There are at command methods whereby the impurities can be completely eliminated with a minimum of operations and cost.

The following may be taken as typical of the composition of these highly purified liquors:—

Zinc	10·00	per cent.					
Copper	·00016	,,	or	1·6	parts	per	1,000,000
Cadmium	·00195	,,	,,	19·5	,,	,,	,,
Iron	·005	,,	,,	50	,,	,,	,,
Manganese	·004	,,	,,	40	,,	,,	,,
Nickel	·00002	,,	,,	·2	,,	,,	,,
Cobalt	·0005	,,	,,	5	,,	,,	,,

(*d*) *Acidification.*—The pure liquor is now mixed with regenerated acid containing 3 per cent. zinc and 10·5 per cent. acid from the electrolytic cells to give a composition approximating to:—

Zinc	8 per cent.
Sulphuric acid	3 „

with a view to economic electrolysis.

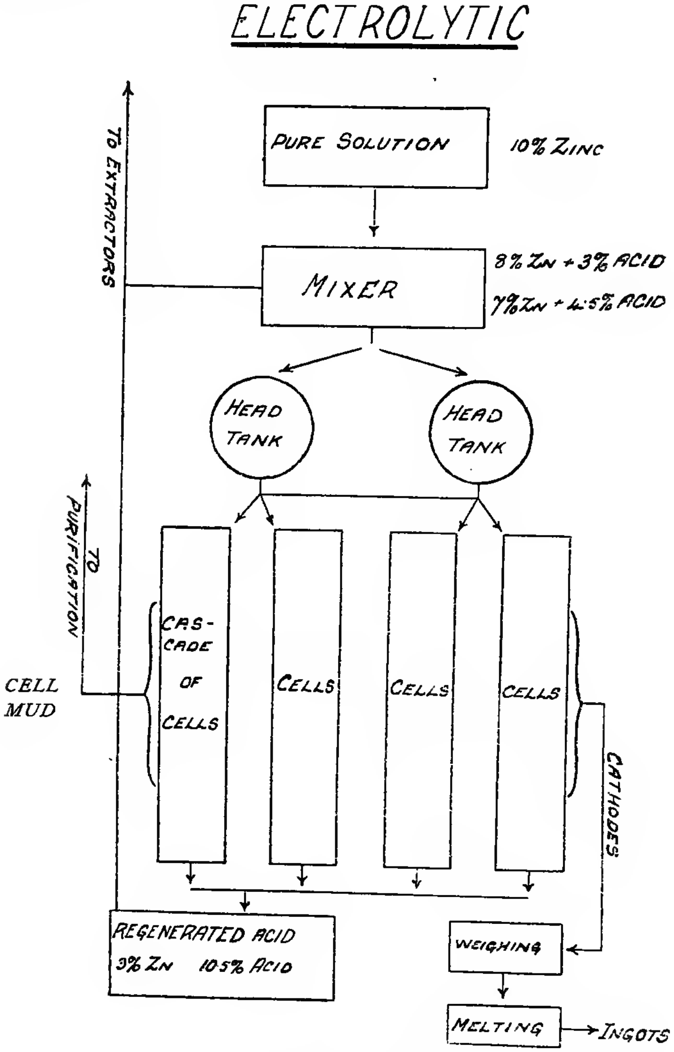

Fig. 2.—Electrolytic Process.

(*e*) *Electrolysis* is effected between lead anodes, which are exceedingly permanent under normal care, and aluminium cathodes from which the deposits are readily detached. Fig. 2 shows the arrangement of the electrolytic plant upon which the work was carried out. With an energy consumption of 3200 K.W.H. per ton of cathodes, the zinc content of the liquors is reduced to 3 per cent., the acid increasing to 10·5 per cent. High and economical recovery of zinc results from purity of liquors, and this advantageously limits the volume of liquor in the solution circuit for a given output of the metal, and therefore reduces the plant in which these solutions are treated. When removed and cast the deposited zinc attains a purity exceeding 99·95 per cent. zinc. Of the impurities present, there are not more than ·02 per cent. lead, ·02 per cent. cadmium and ·01 per cent. iron and copper combined.

Thus from the lowest grade and most complex raw materials the highest grade of metal is obtained.

(*f*) *From the residues* remaining after the extraction of zinc from the calcined ore, silver and lead are recovered as argentiferous lead.

In considering the stages seriatim, and in detail, more attention will be given to those sections and methods which are characteristic of the process now applicable for a wide variety of low grade and complex ores.

VII. ORES.

Table No. I. gives the assays of a number of ores which have been used during the present investigation. They cover a wide range both as regards essential and non-essential constituents. The Halkyn ore was a fluoride ore which went without difficulty through the process.

TABLE I.—ASSAY OF ORES.

	Australian Concentrate.	Vielle Montagne.	Burmah.	Tasmanian Copper Co.	Scotch Mine.	Cornish Mine.	Halkyn.	Shropshire.
Zinc .	47·2	33·4	35·4	26·5	22·2	21·6	41·8	36·1
Copper .	·4	trace	trace	·05	trace	·75	trace	trace
Lead .	4·7	1·73	23·4	8·85	4·62	4	2·35	1·5
Silica .	4·9	7·53	11·2	5	48	42·7	13·4	5·9
Iron . .	9·6	15·0	4·2	14·5	4·0	8·2	1·2	2·6
Alumina .	1·5	·42	—	—	2·1	2·67	·03	1·69
Manganese	3·45	1·13	—	—	nil	nil	nil	trace
Lime .	·64	5·1	—	—	3·3	·65	15 (calcium)	2·9
Sulphur .	29·91	21·4	24·3	34	13·36	15·76	18·5	24·56
Arsenic and Antimony	traces	trace	—	—	trace	trace	—	present
Cadmium .	trace	trace	—	—	present	trace	trace	present
Nickel .	trace	—	—	—	present	present	—	present
Cobalt .	nil	—	—	—	present	present	—	present
Silver (ozs.)	10°	—	20·45	8·46	2	2·8	—	—

QUANTITIES OF ORES REQUIRED.

Assuming (*a*) 94 per cent. zinc made soluble by calcination.

(*b*) Mechanical and handling losses based on one unit per ton 50 per cent. Blende. Operating losses referred to depreciated zinc value of original ore.

TABLE II.

Per Cent. Zinc in Raw Ore or Concentrate.	Less Mechanical Losses.	After Calcination Zinc Soluble.	Per Cent. Extraction of Soluble Zinc.	Zinc in Solution per Ton Ore.	Tons Ore per Ton Zinc in Solution.
50	49	46·06	95	·4375	2·28
48	47·04	44·21	93·4	·4129	2·42
46	45·03	42·37	91·8	·3889	2·57
44	43·12	40·73	90·2	·3655	2·73
42	41·16	38·69	88·6	·3427	2·918
40	39·2	36·84	87·0	·3205	3·12
38	37·24	35·00	85·4	·2989	3·34
36	35·28	33·16	83·8	·2778	3·6
34	33·32	31·32	82·2	·2574	3·88
32	31·36	29·47	80·6	·2375	4·21
30	29·4	27·63	79	·2182	4·58

It need hardly be pointed out that the higher the percentage of zinc in the ore the greater will normally be the recovery in the extraction process due to the greater ease and success in washing out soluble zinc in the smaller bulk of residues, from which also a more effective recovery of lead and silver (and gold if present) can also be attained with simpler treatment.

With a 40 per cent. concentrate—a value much lower than that usually treated by distillation—a little more than 3 tons of ore would be required per ton of zinc produced, representing an overall recovery of over 80 to 85 per cent. The separate losses amounting to 15 to 20 per cent. are in two cases shown herewith, the percentage of zinc after each stage being represented as diminishing percentages of zinc in the raw ore:—

Case I.

Concentrate	40	per cent.	zinc total.
After mechanical losses of grinding and transportation	39·2	”	” ”
Converted to soluble zinc by calcination	36·84	”	94 per cent. being rendered soluble.
Soluble zinc extracted as zinc in the solution	32·05	”	With an 87 per cent. extraction.
Tons ore per ton zinc in solution	3·12	”	With total conversion of zinc into solution of 80 per cent.

Case II.

Concentrate	40	per cent.	zinc total.
Mechanical losses in grinding, etc.	39·2	”	” ”
Converted to soluble zinc by calcination	37·86	”	96·6 per cent. being rendered With e.
Extracted as zinc in solution .	34·16	”	a 90 per cent. extraction.
Tons ore per ton zinc in solution	2·93	”	With total conversion of zinc in solution of 85 per cent.

These figures are taken from actual plant tests and indicate the measure of success attending this the first and an important stage in the process.

VIII. Calcination.

The ores usually treated are of the sulphide type, and as a preliminary operation require calcination, though on lines differing somewhat from those followed in the case of calcination prior to distillation. In the latter case every attempt must be made to reduce the sulphur content to a minimum as each percentage of sulphur remaining in the calcined product whether as sulphide or sulphate holds up 2 per cent. of zinc in an irreducible form.

The temperature employed for this "oxide" roast for distillation, is 800° to 1000° C. with a fuel consumption of about 10 per cent. or less of the weight of the ore calcined, although the calcination is theoretically an exothermic operation. The types of furnace, muffled and open, hand rabbled or mechanical, do not now call for comment. Sulphur is largely expelled as sulphur dioxide which up to the present has been passed on to sulphuric acid chambers, large quantities of acid arising from this source of sulphur. The great risks associated with a high temperature roast are the tendencies to the production of ferrites and silicates.

The electrolytic process is, as will be realised, mainly concerned with handling zinc sulphate solutions, and in one stage at least it becomes necessary to effect complete neutralisation of the last traces of acid by the addition of whiting. This, however, involves the loss of a little acid as calcium sulphate. To this may be added unavoidable losses in handling the liquors in subsequent stages. In maintaining the volume and composition of the liquors these losses would ordinarily be made good by the addition of new acid. An obviously far better course of procedure is to effect calcination at such a temperature as to yield zinc sulphate (soluble in water) in amount sufficient to introduce combined SO_4 equal in quantity to that unavoidably lost in subsequent stages. This is effected at a temperature of 600° to 650° C., beyond which the calcination temperature is not allowed to go. To this type of roast the descriptive term of "sulphate roast" is applied. At this comparatively low temperature there is a much reduced tendency to the formation of what are called "ferrites" compounds of zinc and iron oxides, approximating to the composition of franklinite and which do not so readily yield up their zinc to the acid liquors used in subsequent extraction. Further the low temperature roast militates with advantage against the production of zinc silicate which introduces its own special and not insignificant difficulties attendant upon the presence of soluble silica. These points are of determining importance in the subsequent extraction of zinc, and we are assured that lack of success in some attempts at the electrolytic zinc industry has been partly attributable to the want of appreciation of the optimum conditions under which calcination should be effected.

Normally, if an ore is passing through a Delplace furnace the operation covers a period of about 20 to 24 hours while the fuel consumption for a 40 per cent. zinc ore is approximately 12 per cent. The sulphur dioxide evolved may be passed over to sulphuric acid plants, but it will be obvious that a calcination process which would yield the sulphur of the pyritic ore in the elementary form would constitute a marked improvement in the operation in view of the dearth of natural sulphur in this and other countries. Experimental work is proceeding on an alternative process.

Changes of weight during calcination do not call for comment, but the usual slight increase in the percentage of zinc in the "calcine" will be readily appreciated. After calcination the ores or concentrate may with advantage be reground, reducing it to about 20 mesh.

The compositions of a number of calcined ores are summarised in Table III., embodying the more important works data.

TABLE III.—Assay of Calcined Ores.

	Australian Concentrate.	Vielle Montagne.	Burmah.	Tasmania Copper Co.	Scotch Mine.	Cornish Mine.	Halkyn.	Shropshire.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Zinc total . .	47·47	37·2	34·7	31·8	22·18	20·18	42·1	35·8
Zinc soluble .	46·06	31	32·6	26·9	19·8	19·79	41·2	34·6
Zinc as sulphate	5·6	2·4	4·0	5·1	1·67	9·1	·6	3·5
Lead total . .	5·6	—	21·49	9·95	4·6	—	—	·83
Lead as sulphate	5·4	—	—	—	—	—	—	—
Lead as oxide .	·2	—	—	—	—	—	—	—
Silver (ozs.) .	—	—	23	—	—	—	—	—
Zinc (soluble) / Zinc total	98·3	83·3	94·0	84·6	89·27	98·07	97·86	98·63

IX. Extraction.

The term "extraction" is normally used to cover the process of dissolving out the soluble zinc compounds with the acid liquors from the electrolytic cells, and again it is with the process rather than the plant that we are now concerned.

The liquor used for this purpose comes directly from the cell-house and constitutes the zinc sulphate solution which by electrolysis has lost zinc with the corresponding increase in acid content. Putting down the chemical action in the cells in simple terms as follows:—

$$ZnSO_4 + H_2O = \underset{65}{Zn} + O + \underset{98}{H_2SO_4}$$

it will be seen that the deposition of 65 parts by weight of the metal results in the production of 98 parts by weight of acid. In dealing with simple percentages we normally put this proportion in somewhat simpler terms thus:—

Zinc : acid : 65 : 98 or as 1 : 1·5.

Obviously in first starting up the process a pure acid solution is used which may be 9, 10, 12, 15 or 18 per cent. strength. These figures correspond to 6, 6·6, 8, 10 and 12 per cent. zinc respectively when the acid is completely converted to zinc sulphate. Having made tests on liquors with several of these strengths we have for many reasons chosen 15 per cent. acid or 10 per cent. zinc as being the most economical for the process. Some of the principles guiding this choice may be indicated:—

1. In the first place obvious advantages accrue to the employment o the strongest liquors in that comparatively smaller volumes are involved for any given output of zinc, and with smaller volumes the size of plant and number of operations stand to be diminished.

2. As current efficiency in the cells falls off with decreasing zinc content a larger proportion of zinc can be economically extracted in the cell house from a stronger solution.

3. Stronger solutions have better conductance, and this in lowering the P.D. required to maintain any given current density lowers the kilowatt-hour consumption and prevents undue heating of the solution in the cells.

4. Strong solutions of zinc sulphate are, however, apt to crystallise and yield basic compounds on cooling. Further reference will be made to this later.

5. The extraction of more zinc from the stronger solution in the cell house means the production of a correspondingly stronger solution of acid which in turn may and in the absence of pure solutions does militate against current efficiency and promotes corrosion.

6. Stronger solutions involve a smaller consumption of reagents per ton of zinc, but

7. Loss of zinc through waste solutions will, however, be more marked in the case of these stronger solutions. Taking these and other points into consideration we have usually operated on a solution with an equivalent acid strength of 15 per cent. and we are convinced that a reduction of this figure to 10 per cent. seriously enhances the difficulties and costs of operation. It may appear more obvious later why these more dilute solutions have been tried, but we are persuaded that the difficulties, to overcome which, these more dilute solutions have been employed ought never to occur and do not when the methods, especially those of purification here described are intelligently carried out.

The following approximate compositions represent the solution at the different stages of the process:—

(*a*) Starting acid 15 per cent.
(*b*) Neutral zinc sulphate 10 per cent. zinc.
(*c*) Acidified for electrolysis 8 per cent. Zn, 3 per cent. acid.
(*d*) Outflow from cells 3 per cent. Zn, 10·5 per cent. acid.

Solution (*c*) made ready for the cells is obtained by the admixture of 5 volumes of (*b*) with 2 volumes of (*d*). In every case percentages refer to grams of zinc or acid per 100 c.c.

As solution (*d*) leaves the cells at a temperature of about 40° C. it is run (with as occasion may necessitate an intermediate storage tank) into the extractor which is provided with steam heating coils or open steam pipe and an agitator. Every endeavour is made to conserve heat and thus economise fuel. To a 5 or 10 ton charge of acid liquor, the finely ground calcine is added with stirring when, owing to the exothermic reaction:—

$$ZnO + H_2SO_4 = ZnSO_4 + H_2O$$

the temperature is raised to 70° C. The temperature is now raised to nearly 100° C. and further additions of calcine are made until the acidity is reduced to ·5 per cent. or less. Concomitantly, copper, cadmium, arsenic, antimony, bismuth, iron, manganese, nickel and cobalt pass into solution, lead remaining in the residues as sulphate. At the same time some silica passes into solution as many workers in zinc hydrometallurgy know to their cost. To completely neutralise the acid liquor with calcine would be difficult and wasteful. A rapid neutralisation can be effected by the addition of limestone or whiting. The acid thus neutralised, however, is lost as calcium sulphate, and this course should only be adopted for last traces. In 1916 a patent[1] was granted to Sulman and Pickard for the method of completing the neutralisation by means of zinc hydrate or carbonate obtained by precipitation of otherwise waste zinc liquors with lime or whiting. While the combined sulphuric acid was similarly lost, zinc, in too dilute a form to be put directly into the solution circuit, was recovered.

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[1] British Patent, 104,697, 1916.

As in the subsequent process of eliminating iron, the "iron precipitate" contains some zinc hydrate, we may utilise this precipitate to bring down acidity to about ·1 per cent. which is then completed by limestone, involving the minimum loss of acid. When using iron precipitate very little if any of the iron passes back into solution.

Gels.—To anyone conversant with the properties of colloids and their precipitation as gels some idea of the possibility of silica gel formation will be easily conceived. At this stage of the process some of these solutions if cooled, as would ordinarily occur during filtration, deposit silica gels of such consistency as necessitates the solution being dug out rather than run out. Even if the gel is thin enough to run out, so gelatinous a precipitate very considerably hinders filtration and holds up large quantities of soluble zinc which cannot readily be washed out. The avoidance of these gels constitutes an important problem of zinc hydrometallurgy. When not removed they hold up sufficient zinc in a soluble form to justify an attempt at recovery by drying and dehydrating the gel at a temperature of 150° C., thus rendering the silica completely insoluble and granular. From the desiccated residue the soluble zinc could then be more easily washed out. Gel formation constituted one of our early troubles and these early experiences have, we know, been shared by others. We now effect the complete elimination of gels by adding a slight excess of whiting (the excess amounting to about 10 lbs. per ton of solution) over that required for complete neutralisation and giving the liquor a short period of boiling. Soluble silica is precipitated by quite small additions of alkaline earth carbonates, and the method has been found to be completely successful. To cover this operation a patent[1] has been granted.

Pulping.—The contents of the extractor are now discharged into a pulper in which the residue is kept in suspension by agitation while filtration proceeds. From the filter presses the zinc sulphate liquor usually comes away with a little more than 10 per cent. of zinc owing to slight evaporation, and a judicious washing of the press cake with hot water recovers the water soluble zinc held up in the residue and reduces the main liquor, to which the washings are added, down to the normal 10 per cent. zinc.

Extraction.—The term extraction carries also a quantitative idea of the percentage recovery of soluble zinc in the extraction process. The following example from works daily log sheets will indicate how this value is obtained. Diverse methods are employed and two are illustrated with comments:—

Example.

Regenerated acid used (3 per cent. zinc) } = 5 tons and contain ·15 ton zinc

Ore used, containing 46 per cent. *soluble* zinc, 5 per cent. as sulphate. } = ·85 ton and contains ·391 ton soluble zinc

Total zinc involved in the reaction = ·541 ton.

Tons liquor produced containing 10 per cent. zinc } = 5 tons = ·5 ton zinc.

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[1] British Patent No. 152,752, 1919.

By some, the extraction is set down as

$$\frac{\cdot 5}{\cdot 541} = 92\cdot 4 \text{ per cent.}$$

We prefer, however, to regard the extraction process as the conversion of soluble zinc in calcined ore into zinc in solution and thus the extraction becomes:—

$$\frac{\cdot 500 - \cdot 15}{\cdot 391} = \frac{\cdot 350}{\cdot 391} = 89\cdot 5 \text{ per cent.}$$

and it is on this more conservative method that we state our extractions.

Basic Compounds.—Very little trouble has been experienced with basic zinc sulphate. In order to maintain continuity of operation it became necessary to provide storage tanks between each stage, and in one of these on one occasion the reason for a big deficit in zinc in the daily balance sheet which was regularly kept became apparent. We were at the time experimenting with a 12 per cent. zinc solution. This hot solution on cooling down deposited crystals which after careful washing and drying gave an assay from which they appeared to contain calcium sulphate, with a basic compound described by Roscoe and prepared by boiling zinc oxide with zinc sulphate. To this compound the formula

$$SO_2 \,.\, (O \,.\, ZnO\ Zn)_2O \,.\, 2H_2O$$

has been given.

X. Composition of Crude Zinc Sulphate Solution.

In the outline of the process we gave an approximate idea of the composition of the crude zinc sulphate liquor. Needless to add this varies with each different ore but the data may now be amplified by several analyses taken from the records:—

TABLE IV.—Composition of Crude Zinc Sulphate Solution.

	From Australian Concentrates.	From Mixed Complex Ore.	From Newton Stewart Ore.
	Per Cent.	Per Cent.	Per Cent.
Zinc	9·57	10·0	10·34
Copper	·0354	·057	·0065
Cadmium	·0183	·037	·027
Iron	·01	·05	·0106
Lead arsenic Antimony tin	Traces.	—	—
Manganese	·15	·089	·016
Nickel	·001	·001	·001
Cobalt	Trace.	·0025	·003

XI. Purification.

A. Influence of Impurities in Crude Zinc Sulphate Liquors.—The following impurities usually occur in the crude zinc liquors: copper, arsenic, antimony, bismuth, cadmium, iron, manganese, cobalt, and nickel. Mention might also be made of traces of aluminium, calcium sulphate, lead sulphate, and other substances arising from the treatment of very complex ores with acid.

The elimination of many of these impurities constitutes the most important step in the whole process as the effects of a number of these metals are altogether out of proportion to the percentages usually occurring, and constitute the chief difficulty in the subsequent electrolysis. Any attempt to obtain a commercial zinc deposit from these solutions would be futile. From pure zinc sulphate solutions, the successful deposition of zinc is a matter of comparative ease. From zinc liquors containing quite small, perhaps even under ordinary analytical methods undiscoverable, amounts of certain insidious impurities, the successful deposition of zinc is a sheer impossibility. By some workers it has been regarded that the zinc electrolytic cell is more sensitive to impurities than the usual chemical methods of detection. While this statement emanates from a laboratory of such world-wide reputation as that of the General Electric of Schenectady we feel we must disagree with it and upon the evidence which will be adduced. In one works the suitability of purified zinc liquors for electrolysis was determined by by-passing some of the liquor flowing into the cells through a small test cell in which conditions were arranged so that defects would be quickly revealed. It has been stated "that a variation of between ·001 gram antimony per litre (1 part per million) and ·0003 gram per litre (·3 part per million) made the difference between impossible and excellent cell room operations". Amongst these most detrimental impurities are nickel and cobalt, to the behaviour and elimination of which special attention has been paid. The behaviour of each notable impurity may be briefly stated.

Copper in the electrolyte enters by deposition into the ultimate composition of the zinc, and in the electrolytic process, sets up a marked corrosion which considerably lowers current efficiency and thus increases the kilowatt hour consumption per ton of metal. Owing to its very electronegative character, copper is usually deposited out in the upper cells of a cascade. There the acid content is comparatively low and the temperature too. This, to some extent, limits corrosion as acidity and increase of temperature are the conditions most conducive to corrosion. If a piece of copper wire crudely touching zinc under acid rapidly promotes corrosion, the effect of the molecular contact between the two metals occasioned by simultaneous deposition may well be conceived. The results are indeed disastrous.

Cadmium left in the electrolytic liquors passes almost completely into the zinc deposit without inducing visible or appreciable corrosion. From the known amount of this metal in the liquors and the proportion of zinc which is being extracted therefrom, a very fair estimate of the percentage of cadmium in the deposited zinc may be made. Cadmium imparts brittleness to zinc. The removal of cadmium from the liquors is not quite so simple as might at first be imagined, and the allowable quantities of metallic impurities in the final product determine the degree to which the elimination must take place. In this connection it may be stated tha tthere is all the difference in purification procedure in two cases in which only a 99·9 per cent. metal is aimed at (as in America) or a 99·95 per cent. metal, as the standard which was somewhat arbitrarily set in Great Britain, but to which, nevertheless, we had no difficulty in attaining.

The relation between the quantities of cadmium in the liquors and final zinc is shown in Table V., in which each experiment started with approximately an 8 per cent. zinc and 3 per cent. acid electrolyte.

TABLE V.

	Electrolyte after Deposition.		Per Cent. of Cadmium in	
	Per Cent. *Zn.*	Per Cent. H_2SO_4.	Starting Solution.	Cathode *Zinc.*
1	2·6	11·52	·003	·06
2	2·73	11·20	·006	·12
3	3·5	9·7	·01	·17
4	3·5	9·75	·02	·35
5	3·1	10·4	·10	1·62
6	3·15	10·1	·20	3·61

In each case, only a trace of cadmium remained in the liquor, and this, with the fair proportionality between the two sets of figures for cadmium, at once impresses the lesson of the most desirable freedom from cadmium of zinc sulphate liquors for electrolysis.

Arsenic, Antimony, and Bismuth are usually met in only very small amounts. Their effects in the zinc cell may be well imagined from their position in the electro-chemical series, in virtue of which fortunately, they are amongst the easiest and first of the impurities to be removed, and a solution freed from copper can contain no notable amount of these impurities.

Aluminium frequently occurs in the liquors. It is not subject to electro-deposition. It does not induce corrosion, in fact, aluminium sulphate has been added in some applications of zinc electrolysis to enhance the nature of the zinc deposit. Without detrimental effect and possibly with advantageous effect, the metal cannot accumulate as the removal of iron from the liquors simultaneously effects the removal of aluminium.

Manganese very frequently occurs. It appears to be a welcome impurity. Occurring as the sulphate it is rapidly oxidised at the anodes to permanganic acid, which, at an elevated temperature, reacts with the sulphate and precipitates a nearly black hydrated manganic oxide. This is a well-known analytical reaction.

On one occasion the same liquor flowing down two series of cells, one of asphalted concrete and the other of wood, and under the same electrical conditions, behaved very differently as regards colour. The liquors in the concrete cells became violet. That in the wood cells was almost colourless. The wood cells conserved heat and the temperature of reaction between the two manganese compounds was soon attained. The concrete cells kept cooler by radiation, and maintained the colour of the oxidised manganese compound. At one time we suspected that the presence of a deep permanganate colour might appreciably depreciate current efficiency, but subsequent test revealed no such defect. Normally, manganese is thrown down as a higher oxide in the form of a mud at the bottom of the cells, and mixed, as it is, with anodic lead peroxide, constitutes an important purification reagent as will be explained later.

Iron.—The presence of iron in the liquors is not to be wondered at, and much depends upon the ultimate degree of purity aimed at as to the necessity for limiting it in the electrolyte. When present in small amounts it does not pass into the deposit. With very appreciable quantities it might be traced into the cathode zinc. Its detrimental effect lies in its lowering the current efficiency by alternate anodic oxidation and cathodic reduction. It is, however, susceptible to ready elimination and constitutes no serious factor in the process.

In our early experience of some of the ores which came under investigation, only the above mentioned impurities were met, and these, fairly readily removed, left solutions from which very satisfactory and thick deposits of three days continuous running were obtained. We had yet to realise that it is only through much tribulation that we should enter the kingdom of complete success. A change of ore brought new phenomena. After the usual purification, the solutions were yielding very satisfactory deposits, when to our consternation a most marked type of corrosion of the cathode zinc was set up. Large and deep holes appeared and quickly developed on already thick plates, and, as the acidity and temperature of the liquors increased, the bulk of the deposit was redissolved. A search for the cause of this evil at once began. It was at first suspected to be due to particles of lead peroxide floating in the electrolyte and attaching themselves to the cathode. In pure liquors, however, an abundance of lead peroxide failed to reproduce the effect. Systematic additions of traces of impurities were made to pure zinc sulphate solution, and the observed corrosion effects recurred when cobalt salts were the impurities added. When the elimination of cobalt from the liquors had been most satisfactorily effected, an altered type of corrosion now became obvious. This was eventually traced to nickel. These impurities merit special mention.

Nickel and Cobalt.—It has, we believe, been suggested that one of the insurmountable difficulties of zinc electrolysis was that, even when starting with a comparatively pure liquor, the cyclic operations led to the solutions "going on the booze," in other words, the balance of conditions became upset by the solution acquiring some constituents which were not ordinarily removable, and which wrought disastrous effects on the electro-deposition. While undetected and unremoved and therefore accumulating, quantities of nickel and cobalt might well deserve this denunciation, still, we are convinced that in this case at any rate, the road to success lies along the path of prohibition, by the application of the newer methods of purification which will now be indicated.

So disastrous are the effects of cobalt and nickel that quite a few parts of either metal per million parts of liquor very markedly reduces the efficiency of the cell house operation, and to a point below what can be called economic recovery. Yet in the behaviour of these two impurities there is a marked divergence. In the first place cobalt does not pass into the cathode zinc, and apart from elimination during purification, it accumulates and constitutes a "cumulative" impurity, accumulating slowly in quantity, but rapidly as regards effects. The corrosion it promotes consists of pinholes in the deposit penetrating the thickness of the deposit and then leading to a corrosive effect at the back of the deposit accompanied by a black stain on the deposit. This concealed corrosion proceeds very rapidly.

By way of contrast it may be stated that, occasionally, it has been possible to detect nickel in the deposit, but never in such amount as would seriously interfere with the ultimate composition. But nickel is even more disastrous as regards corrosion, which however is of a totally different type from that of cobalt. On a comparatively good plate small holes appear. These, unlike those due to cobalt, widen, and a deep, sharp and clean hole is cut right through to the aluminium starting sheet. So marked are the differences between the two types of corrosion that they could readily be detected by feeling deposits with the eyes shut, and thus there is some justification for the claim of the possibly greater sensitivity of the zinc cell for certain, especially these impurities, though we must confess that our developed methods of detecting these metals would lead us in every case to accurately forecast whether the usual types of corrosion would occur with any given liquor.

B. REMOVAL OF IMPURITIES.—Up to the time of the discovery of cobalt and nickel as disturbing elements, a very simple line of purification had been employed, and the ores had been of a very amenable type.

De-ironisation.—After extraction and separation of the zinc liquors from the residues, iron was removed by raising the temperature of the solution, adding whiting and blowing in air. The operation is termed "*de-ironisation*". Iron is precipitated as ferric hydrate, the precipitate carrying some manganese and also basic zinc compounds. This "iron precipitate" was used again in reducing the acidity in the extractors to effect the recovery of its zinc, very little or none of the iron passing back into the liquors in the last stages of neutralisation. De-ironisation was facilitated by the presence of manganese salts, which doubtless act catalytically. The operation was a simple one and will be referred to again.

Copper and Cadmium were next removed by either tube-milling with zinc balls or agitating the neutral liquor from de-ironisation with zinc blue. Copper, and with it arsenic, antimony and bismuth are readily removed, though somewhat greater difficulty was experienced with cadmium. Normally the liquors were then passed forward for electrolysis, but the discovered presence of cobalt introduced a new stage in the purification process.

Precipitation of Cobalt was first and for a long time very successfully affected by boiling the cobaltiferous liqour with lead dioxide,[1] manganese dioxide, or the mixed oxides constituting cell mud. The reactions presumably take the following course:—

$$2CoSO_4 + PbO_2 + H_2O = Co_2O_3 + H_2SO_4 + PbSO_4$$
$$2CoSO_4 + MnO_2 + H_2O = Co_2O_3 + MnSO_4 + H_2SO_4$$
$$3CoSO_4 + PbO_2 + 2H_2O = Co_3O_4 + 2H_2SO_4 + PbSO_4.$$

Lead peroxide as a by-product of accumulator manufacture was found to be a suitable and economic material. Usually it contained:—

65 per cent. PbO_2
35 per cent. $PbSO_4$

and was used in the proportion of 1 part to 200 parts of liquor The mixture was gently stirred by agitators or compressed air and the reagent could be used several times before being passed to the lead plant for the recovery of the lead. The cost of materials for this operation was therefore of a trifling character. We were thus able to reduce the cobalt in the liquors down to 5 parts per million, an amount which was, by experience, determined to be quite allowable in the cells. Other oxidising agents such as sodium hypochlorite and bleaching powder were available, but these introduced undesirable constituents, such, for example, as chlorine, into the liquors and had thus to be rigidly avoided. On the works plant it was usual for the head of the electrolytic section to test the "de-cobaltised" liquor before its acceptation.

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[1] British Patent No. 138,948.

The *Removal of Nickel* was for some time effected by practically boiling the solution with zinc blue. Again the proportion of reagent was 1 part to 200 of liquor and could be used several times over especially with slight additions of new "blue". While this reaction was fairly satisfactory and served for some time, it left something to be desired in that it tended to the production of basic zinc sulphate which slowed down the reaction and also involved loss of zinc. At the same time, the removal of nickel was accompanied by the removal of traces of cadmium which had escaped in tube milling, or on the treatment with zinc fume at lower temperature. It must be stated that temperature was a determining factor in nickel and cadmium elimination.[1]

Thus far, we had processes which reduced every impurity to within the very narrow limits permissible in the highly sensitive zinc cell. But as stand-by plant is an essential to secure continuous production in spite of emergencies, so it was felt that alternative, and if possible, improved processes should be available for essential output of pure liquors. With that decision further research work was at once undertaken. It must be recognised however that the very special nature of the zinc electrolytic cell limits the choice of purification reagents, for no materials can be employed which would impart any constituent to the solution which might have a detrimental effect during electrolysis either at the cathode or even at the lead anode. How this guiding principle was followed will be seen in subsequently developed methods. Thus purification agents might be (1) gases which during reaction would be self-eliminating; (2) metals of such electro-negative character that they would again be, in the presence of a more positive and allowable metal, eliminated, or (3) metals of more positive nature than zinc and thus not deposited with it though capable of elimination to avoid considerable accumulation. Practically the whole of the impurities of zinc solutions are eliminated by one of two general methods, *viz.*, oxidation and reduction. Cobalt as an exceptional case may be removed in both ways. Reference has already been made to the use of air in oxidising out iron and lead peroxide for cobalt, while zinc fume constitutes a reducing agent in the elimination of copper, cadmium, arsenic, nickel, etc. Modifications of the scheme outlined above will be especially welcome if the number of operations can be reduced by the simultaneous removal of two or more impurities.

Use of Ozone.—Ozone or ozonised air is known to be a powerful oxidising agent. It fulfils every requirement of the special conditions attaching to electrolytic zinc sulphate solutions and may be regarded as one of the cheapest purification agents which can be used. Patent rights have therefore been granted in this and other countries covering the use of ozone or ozonised air.[2] The particular impurities removed are those which are susceptible to oxidation such as iron, cobalt, arsenic, and antimony. Ozonised air is easily and cheaply produced, readily distributed and combines both functions of purification and stirring agent. It may here be pointed out that oxidised manganese compounds are very effective in the removal of iron from zinc liquors. Normally the crude zinc liquors contain manganese, sometimes as much as ·15 per cent. of the metal. This is in the manganous or relatively inactive condition. Even in neutral solution, ozonised air precipitates manganic compounds, but this action proceeds apace in the presence of a little alkali like lime which precipitates the manganese in a form readily susceptible to oxidation. This is effected by ozone when :—

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[1] British Patent No. 138,947.

[2] British Patent No. 138,946.

$$2MnSO_4 + 2Ca(OH)_2 + O_3 = Mn_2O_3 . H_2O + 2CaSO_4 + H_2O + O_2$$

or $$6MnSO_4 + O_3 + 6Ca(OH)_2 = 3Mn_2O_3 . H_2O + 6CaSO_4 + 3H_2O.$$

The effect of manganese compounds on iron is too well known to necessitate further reference. With the precipitation of iron, arsenic and antimony come down, in the former case as a basic ferric arsenate. With cobalt compounds the oxidation appears to proceed upon the following lines :—

$$2CoSO_4 + Mn_2O_3 . H_2O = Co_2O_3 . H_2O + 2MnSO_4.$$

The cobalt is precipitated as a higher oxide while the manganese in the absence of alkali or alkali carbonate would revert to sulphate. Manganese compounds thus act catalytically, and if any addition is made for this purpose only manganous compounds need be added while other patent specifications covering the addition of manganese compounds specify the more highly oxidised compounds.

There are a number of types of efficient ozone generators available, and the normal product contains 2000 parts of ozone by volume per million of air. The ozonised air is used at an elevated temperature and serves a most effective purpose in bringing the elimination of cobalt within the scope of the de-ironising operation.

Use of Zinc Blue in Acidified Solutions.—The remainder of the impurities can at once be eliminated by the application of zinc blue to the acidified solution.[1] In a neutral solution the use of zinc blue is attended by the difficulty of the production of basic zinc sulphate. If this type of purification partakes of the nature of electro-chemical action, as indeed it must, it would appear to be considerably facilitated by the addition of a small amount of acid and this we find to be the case. The liquors to be purified are heated to 96° C. and sufficient acid, either new or regenerated from the cells, is added to bring the acidity up to ·1 per cent. Zinc blue is now added in stages and the solution agitated. The amount of blue powder required varies with the quantity of impurities. Normally ·2 per cent. suffices. The acid varies with the quantity of zinc blue. An equal weight of 50 per cent. acid is added previous to the addition of zinc blue. In any case an excess of zinc is used, of which an amount equivalent to the acid present and the impurities removed passes into the solution and is subsequently recovered as electrolytic zinc. The sludge containing the impurities such as copper, cadmium, and nickel may be used again, but where cadmium is present, will in time, pay for the costs of the extraction of cadmium.

Of the impurities thus eliminated cadmium offers the greatest resistance and copper the least. Usually, however, when the nickel has been reduced to an amount which shows no interference with electrolysis, cadmium has been lowered to a degree which has no detrimental effect on the composition of the resulting zinc. Further, this purification proceeds more rapidly in the presence of appreciable amounts of copper, and while this metal is usually present in the ores treated, experience has dictated the desirability of adding a little copper salt to the solution in order to facilitate purification. The copper may be added as an oxide or carbonate ore during extraction, and needless to add, it is entirely removed during the purification. In this process the consumption of acid does not come up for consideration. Measured over a number of consecutive tests on 5-ton lots of liquor the consumption of zinc powder was 0·2 per cent. A simple calculation having in mind that much of the zinc is recoverable, will show that this process of purification is not one of great cost.

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[1] British Patent No. 138,954.

Mercury as a Purification Agent.—As the elimination of copper, cadmium, and nickel is essentially a process of substitution by electrochemical means it is obviously desirable to use two metals in contact which are widely separated in the electro-chemical series and which thus exhibit great electro-chemical activity. If metals or metallic salts are used they must be such as will entirely be eliminated simultaneously with the impurities, or, if they persist in the solution, not unduly accumulate, and, in any case, exert no detrimental effect on the zinc deposition. At the negative and positive ends of the series mercury and aluminium respectively offer possibilities. The greater activity of the aluminium-mercury couple over the zinc-copper couple in organic reductions is well known and led to an attempt to remove deleterious impurities by similar means. On the small scale clean aluminium or zinc (or an alloy of the two metals) turnings are passed through a weak mercury solution. The metals become amalgamated and in this condition are exceedingly active. Placed and stirred in a crude zinc sulphate solution, preferably faintly acidified, the amalgamated metals at once bring about the elimination of practically all impurities except iron. Interest will centre round the use of mercury against which hydrogen has a cathodic over-voltage quite equal to that of zinc and hence the permanence of amalgamated zinc in sulphuric acid. This difficulty of depositing hydrogen up against mercury advantageously acts in the greater comparative facility of the deposition of the negative metallic impurities.[1]

Alternatively, mercuric sulphate, in an amount not exceeding ·005 to ·01 per cent. of mercury in the zinc solution, may be added followed by blue powder. At an elevated temperature, and with agitation, purification from all detrimental metals save iron is quickly effected with a consumption of zinc blue not exceeding ·2 per cent. reckoned on the solution. The method therefore offers commercial possibilities and work is proceeding as to the minimum quantities of reagents required in this and alternative methods of effecting the essential and high degree of purification.

Fig. 3 shows the scheme for purification in three stages which was followed in the earlier stages of the work.

A Single Stage Purification.—If the standard of electrolytic zinc is set, as in America, at as low a figure as 99·92 per cent. a quicker procedure is possible. The calcine is extracted with acid liquor in the usual manner and the acidity brought down by means of ore to ·5 per cent. If iron precipitate referred to above is available, or zinc hydrate or carbonate from waste liquors is available the acidity may be then reduced to ·1 per cent. At this stage zinc blue is added preferably following the addition of a mercury salt. Copper, cadmium, arsenic, antimony, nickel, and cobalt are eliminated and the solution reduced to neutrality. Addition of limestone is now made for the elimination of gels when with air or ozonised air agitation, iron is quickly reduced to an insignificant amount. After a short boil the whole is discharged into a pulper and filtered or other processes of clarifying the solution used, and the liquor after acidification can at once be passed to the cells.

Tests made on these lines gave a final zinc product of 99·92 per cent.

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[1] British Patent No. 138,950.

zinc and over, and where an unduly high purity is not demanded, the single stage process markedly cuts down purification costs against which, however, something must be set for decreased current efficiency. The reduction of purification costs, include labour, time, decreased plant, and interest thereon, though the single stage process does not lend itself to the recovery of copper and cadmium if present in appreciable amounts. The course of purification to be finally selected will depend upon a balancing of many conditions.

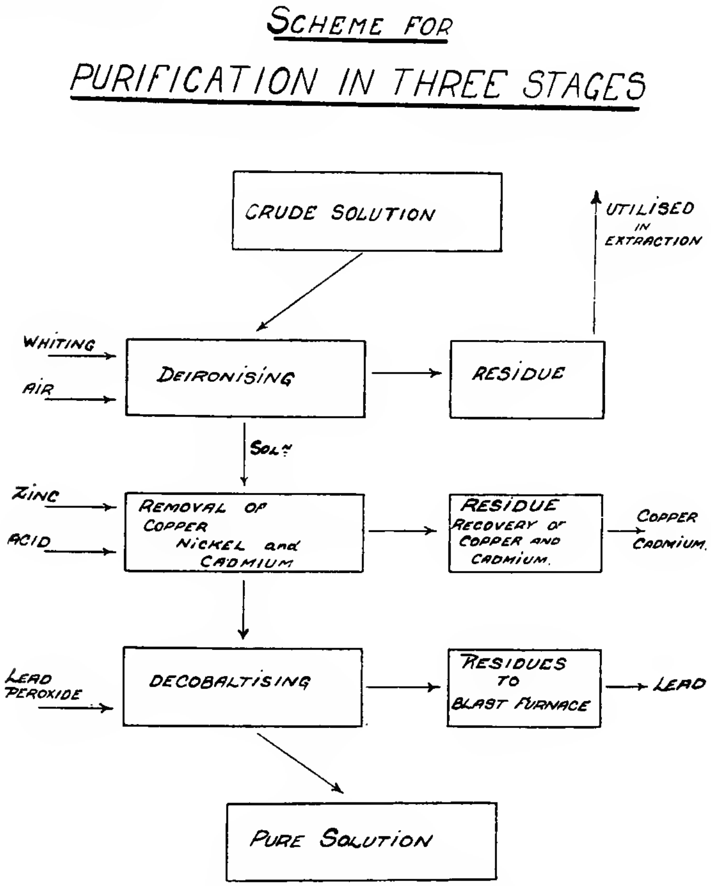

FIG. 3.—Three-stage Purification.

C. ADVANTAGES OF HIGHLY PURIFIED LIQUORS.—The percentage of impurities in crude and purified liquors can now be set out side by side:—

	Crude Solution.	*Purified Solution.*
Copper	·0065	trace
Iron	·0106	·005
Manganese	·016	·0059
Cadmium	·027	·0005
Arsenic Antimony	traces	nil
Nickel	·001	·00002-·00003
Cobalt	·003	·0005

and the advantages of highest degree of purification set out. The limits of the impurities which enter into the composition of the final zinc without marked depreciation of current efficiency will be set by the maximum amount of such impurities allowable in the final product. Those for cobalt and nickel however cannot be so readily determined. They depend upon a number of conditions and costs which can only be balanced as the result of large scale tests. These conditions may perhaps best be indicated by a consideration of an actual case in which somewhat extreme conditions (though well within the range of current practice) are taken. In two methods of operation A and B the liquors in A are sufficiently pure to admit of economic electrolytic recovery of zinc down to 3 per cent. zinc while on B impurities incompletely removed necessitate the liquor outflows passing away with 5 per cent. zinc. Then :—

	A	*B*
Zinc in liquor from purification	10 per cent.	10 per cent.
Zinc in outflow from cells	3 per cent.	5 per cent.
Zinc extracted	7 per cent.	5 per cent.
∴ Volumes liquor to be purified per ton of deposited zinc	14·3 tons.	20 tons.

In fact some of the work has been carried on with a liquor of 18 per cent. acid basis (≡ 12 per cent. zinc neutral), electrolysis being continued until the zinc figure stood at 4 per cent. Thus an 8 per cent. zinc extraction from the liquor represents only 12½ tons of liquor being handled per ton of zinc cathodes. As solution volumes are usually expressed in short tons a slight increase in the above mentioned figures must be made when volumes are under consideration.

XII. Electrolytic.

Introduction.—A good deal of work has been done on the deposition of zinc from points of view other than that of the commercial recovery of the metal. The conditions for the most successful analytical recovery of zinc have been carefully worked out, while the deposition of zinc for electro-galvanising has attained extended and most successful use.

New problems, however, arise in the electrolytic recovery of zinc from sulphate solutions. Large volumes of solutions are being handled and from them commercial economy demands a maximum extraction of the metal. The liquors must be of good conductance and not contain impurities which have a deteriorating and disintegrating effect on the lead anodes which are so largely used. The extraction of the zinc must be effected with the minimum energy consumption where power is dear. Cheaper power, however, may somewhat modify the procedure in view of the combination of this operation with the hydrometallurgical process already referred to. Dense deposits readily detached from the aluminium cathodes and capable of efficient fusion are essential. It may be said that most of these conditions may now be readily realised.

Simple Reactions.—When zinc sulphate is electrolysed with an insoluble, say a lead anode, the following chemical decomposition is effected :—

$$ZnSO_4 + H_2O = \underset{\substack{65\\ \text{at}\\ \text{cathode}}}{Zn} + \underbrace{\underset{16}{O} + \underset{98}{H_2SO_4}}_{\text{at anode}}$$

The deposition of 65 grams of zinc is accompanied by the production at the anode of 98 grams of sulphuric acid. For simplicity of figures the proportion of zinc to acid may be taken as 1 : 1·5 instead of 65 : 98. Thus a 15 per cent. acid may be converted into a 10 per cent. zinc solution while a starting liquor of 10 per cent. zinc will on electrolysis pass through the following stages of composition :—

Per cent. zinc 10, 8, 6, 4, 2
Per cent. acid . . . . . . 0, 3, 6, 9, 12.

Thermochemically the action may be represented

$$\underset{248{,}000}{ZnSO_4 . Aq} + \underset{68{,}360}{H_2O} = Zn + O + \underset{210{,}200.}{H_2SO_4Aq}$$

Gram equation quantities involve the absorption of 106,160 calories with an equivalent decomposition voltage of 2·3 volts. In view of the fact that the decomposition voltage of dilute sulphuric acid and the deposition of hydrogen is only 1·5 volts it would, at first, appear that the deposition of zinc from acid solutions would be not easily possible. The phenomenon of over-voltage here plays a large determining part. It is well recognised that the deposition of hydrogen on a zinc cathode involves an additional voltage or " over-voltage " of at least ·7 volt and this brings the hydrogen separation voltage higher than that for zinc, thus making possible and practicable the deposition of the metal from quite strongly acid solutions. All conditions which influence over-voltage will have a profound effect on zinc deposition from acid solutions. Lowering the over-voltage facilitates hydrogen deposition and vice versa. Elevation of temperature reduces over-voltage of hydrogen, and therefore the current efficiency in terms of zinc deposited. Deposited impurities markedly lower over-voltage and thus give the rise to further inefficiency making it possible for zinc which has already been deposited to be dissolved again by local action. Nickel and cobalt in minute quantities undetectable in the zinc deposit doubtless act in precisely the same pernicious manner. Over-voltage is, however, increased with current density and it is a matter of experience that current efficiency in zinc deposition is raised by an increase in current density with increased acidity. The following figures representing the over-voltage of hydrogen from normal sulphuric acid are given by Caspari :—

Platinised platinum .	·005 volt.	Tin . .	·53 volt.
Smooth platinum .	·09 ,,	Lead . .	·64 ,,
Silver . .	·15 ,,	Zinc . .	·70 ,,
Nickel . . .	·21 ,,	Mercury .	·78 ,,
Copper . . .	·23 ,,		

Similar effects come into play with the oxygen at the anode, the increased difficulty of separating oxygen against lead peroxide amounting to approximately ·5 volt and being to some extent responsible for the markedly increased voltage required to maintain the constant current density in the charging of accumulators.

The separation of hydrogen and oxygen therefore from normal sulphuric acid against a zinc cathode and a lead peroxide anode is of the order of 1·5 + ·7 + ·5 = 2·7 volts as against 2·3 calculated for the decomposition of zinc sulphate.

Very quickly it will be realised that as electrolysis proceeds the following changes of electrical conditions will therefore accrue :—

1. The solution becomes more conductive by reason of increasing acid.

2. Conductivity is further increased by the unavoidable, and, within limits, desirable increase in temperature.

3. These conditions lead to a fall in P.D. in the successive cells through which the liquor may be cascading.

4. Decreasing zinc content will lead to a decreased current efficiency to which some limit of zinc content will need to be set.

5. An elevation of temperature reduces the over-voltage of hydrogen against zinc and thus facilitates evolution of the gas with concomitant decreased efficiency.

6. Similar and even more marked effects occur in the presence of impurities.

These effects can best be realised by inspection of the accompanying typical curves (Fig. 4) plotted with :—

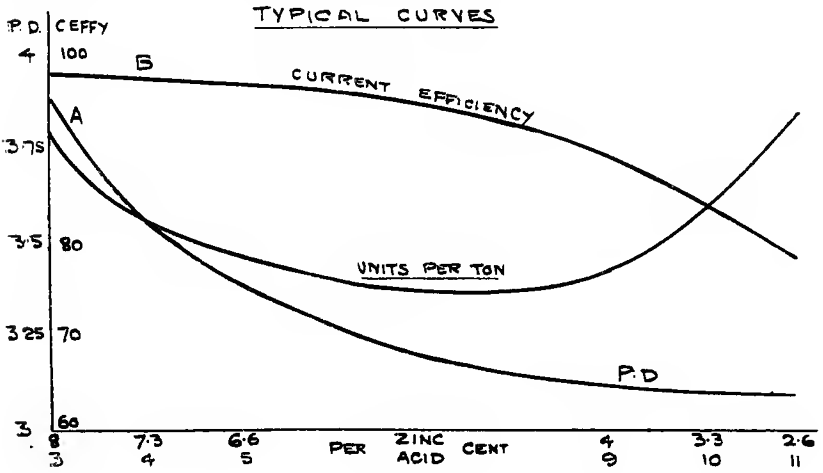

FIG. 4.

Ordinates as P.D. current efficiencies and K.W.H. units per ton, and *Abscissae* as composition of solution.

Curve A shows the type of potential fall.

Curve B illustrates the falling off in current efficiency.

From these two values an expression can be deduced for the energy consumption. From the fundamental Faraday Law of equivalent electrodeposition a constant of the number of ampere-hours required to deposit one ton of metal is obtained.

For zinc this is approximately 840,000.

Then

$$\text{K.W.H. per ton zinc} = \frac{\text{P.D.} \times 100}{\text{C. Eff.}} \times \frac{840000}{1000}$$

$$= \frac{\text{P.D.} \times 84000}{\text{C. Eff.}}$$

Thus 3·35 volts and a 90 per cent. current efficiency, quite normal conditions, represent :—

$$\frac{3{\cdot}35 \times 84000}{90} = 3130 \text{ K.W.H. approx.}$$

These figures refer to what one may justly call pure solutions, and a point of immediate importance is that of the most economic composition of finishing liquor. Taken at the outflow of cell No. 9, Table VI., p. 28, the following figures are calculated:—

$$A\begin{cases}\text{Outflow liquor, 5 per cent. Zn., 7·5 per cent. acid.}\\ \text{Current efficiency (over all)} = 95{\cdot}7 \text{ per cent.}\\ \text{Average P.D.} = 3{\cdot}47 \text{ volts.}\\ \text{K.W.H. per ton} = 3031\end{cases}$$

Again, in a case in which the zinc had been extracted down to 3 per cent., the figures from laboratory notebooks are as follows:—

$$B\begin{cases}\text{Outflow liquor, 3 per cent. Zn., 10·5 per cent. acid.}\\ \text{Current efficiency} = 88{\cdot}8 \text{ per cent.}\\ \text{Average P.D.} = 3{\cdot}32 \text{ volts.}\\ \text{K.W.H. per ton} = 3140\end{cases}$$

The figures for A and B stand as follows:—

	A.	*B.*
K.W.H. per ton zinc	3031	3140
Approximate per cent. zinc extracted from the neutral 10 per cent. solution	5	7
Tons vol. liquid per ton zinc cathode . .	20	14·3

Thus against the apparent saving of 109 K.W.H. per ton of zinc deposited must be set the fact that in A 20 tons of liquor must be taken from the purification plant to yield 1 ton of zinc cathodes as against 14·3 tons in B. Operating according to A will thus demand a daily treatment of $\frac{20 - 14{\cdot}3}{14{\cdot}3}$ = 40 per cent. more liquor for the same output of cathodes. with the proportionate increase in size of plant and other purification costs. Again as regenerated acid passing back to the process plant is a pure liquor which is rendered impure by further extraction, the A operation necessitates the repeated purification of 5 per cent. of zinc in solution as against 3 per cent. in the case of B. These figures serve to emphasise the importance of the extreme desirability of pure liquors, and the comparative results may be much more striking when the liquors contain such quantities of nickel and cobalt as necessitates a higher content of zinc in the outflowing solution. This is, we believe a difficulty which has been experienced in some attempts at a process in which the greatest purity of electrolytic liquors was not attained.

Laboratory Data.—In order to test more accurately than would have been possible on the large plant, the effect of added impurities in the process of electro-deposition, a series of over fifty experiments was made on a laboratory scale. These experiments ran for a period of 24 hours in most cases and in a series of 12 cells arranged in cascade. The zinc deposited in each experiment was of the order of four pounds, and every precaution was taken to ensure accuracy and consistency in the results. In addition to the influence of impurities, other variations of conditions studied included concentrations of electrolytes, current density, inter-electrode space, and temperature. But a few of the results can now be referred to, and these but briefly, as the more important, *viz.* those due to impurities were outlined in a recent paper before this Society.[1]

Table VI. gives a typical series of figures with a pure electrolyte containing 8 per cent. zinc and 3 per cent. acid. During the test 1992 grams of zinc were deposited and the final liquors contained 4 per cent. zinc and 9 per cent. acid. The figures are plotted in Fig. 5, and it will at once be seen that they are of the type shown in Fig. 4.

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[1] *Trans. Faraday Soc.*, Vol. xvi., p. 492.

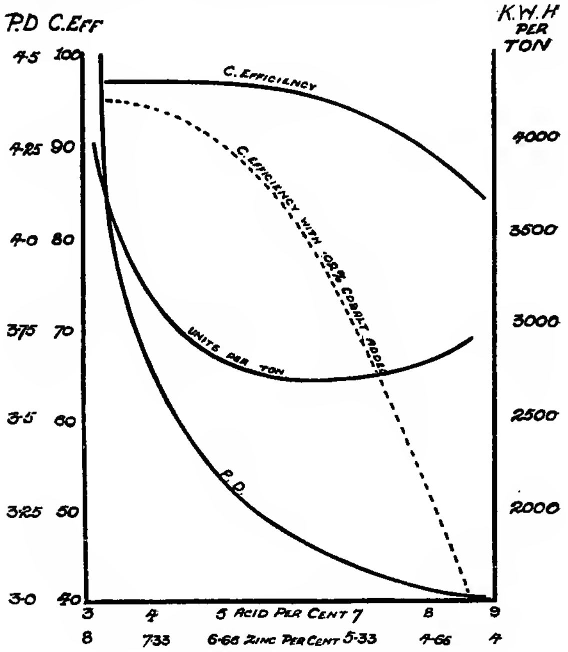

Fig. 5.

TABLE VI.

12 cells in cascade. Solution pure.
Starting liquor Zinc 8·0 per cent. Acid 3·0 per cent.
Outflowing liquor ,, 4·06 per cent. ,, 8·91 per cent.
CD = 28 amperes per square foot.

Cell No.	Zinc Deposit Grams.	Current Efficiency.	P.D.	Average Composition of Liquor.		K.W.H. Per Ton Zinc.
				Per Cent. Zinc.	Per Cent. Acid.	
1	171·7	96·8	4·63	7·83	3·26	3991
2	171·2	96·5	3·69	7·48	3·78	3195
3	171·9	96·9	3·64	7·13	4·3	3139
4	171·7	96·8	3·40	6·79	4·82	2935
5	170·7	96·3	3·24	6·44	5·34	2814
6	169·2	95·5	3·21	6·10	5·84	1810
7	168·6	95·1	3·18	5·77	6·35	2794
8	167·8	94·7	3·17	5·43	6·85	2799
9	165·1	93·1	3·13	5·10	7·34	2810
10	160·5	90·5	3·08	4·78	7·83	2845
11	152·6	87·0	3·04	4·47	8·30	2922
12	150·8	85·0	3·01	4·16	8·76	2959
Averages		93·7	3·37			3001

Many considerations of an economic character arise from data thus obtained. A loss of .1 per cent. in current efficiency means a loss of a ton of zinc per day on a 100 ton plant and a correspondingly larger electrolytic plant for a given output. Energy consumption permissible will be to some extent controlled by the cost of current. Current density simultaneously influences energy consumption and size of plant. While data is available on each of these varying conditions only the briefest treatment is here possible. For the most part an inter-electrode space of 1½ inches and a current density of 28 amperes has been used. In reducing the zinc content of the solution from 8 to 3 per cent. the maximum temperature attained in the lowest cell of a series was from 42° to 45° C.

The influence of cobalt is seen from the following figures obtained with a solution containing ·02 per cent. of this impurity. The case is an extreme one, but is introduced as indicative of the trend of all impurities.

TABLE VII.

Electrical Data in experimental series of 12 cells with solution containing ·02 per cent. of Cobalt.

Cell No.	Zinc Deposit, Grams.	Current Efficiency.	P.D.	Average Composition of Liquor.		K.W.H. Per Ton Zinc.
				Per Cent. Zinc.	Per Cent. Acid.	
1	134·9	95·5	5·28	7·79	3·31	4620
2	132·8	94·0	3·4	7·38	5·93	3022
3	128·5	91·0	3·25	6·97	4·54	2985
4	127·5	90·3	3·23	6·58	5·13	2962
5	127·4	90·2	3·20	6·19	5·72	2983
6	105·0	74·4	3·20	5·83	6·26	3597
7	103·2	73·1	3·17	5·50	6·74	3603
8	94·6	67·0	3·15	5 20	7·19	3955
9	82·2	58·2	3·15	4·93	7·60	4523
10	80·1	56·7	3·13	4·68	7·98	4612
11	62·3	44·1	3·09	4·46	8·31	5855
12	59·05	41·8	3·09	4·27	8 59	6177
Averages		73·0	3·36			4074

These current efficiency figures are shown by a dotted line in Fig. 5 which admits of easy comparison with those of a pure solution.

With ·001 per cent. cobalt, a quite usual amount on zinc liquors, the following comparative figures were obtained :—

Current Efficiency . . . . . 83·5 per cent.
Units per ton . . . . 3285.

The influence of nickel is equally if not even more marked, but the results are very much improved by the addition of a colloid such as dried size. This is shown in the following figures :—

Liquor Containing			
·0005 Per Cent. Ni.		·0005 Per Cent. Ni. and ·0005 Per Cent. Dried Size.	
Current Efficiency 88·7	K.W.H. per ton 3099	Current Efficiency 94	K.W.H. per ton 2898

The data for the two current efficiencies are plotted in the curves in Fig. 6.

XIII. Energy Consumption.

To an average figure of 3200 K.W.H. per ton of cathode zinc—a figure which with care could be reduced—we add an ample electrical power consumption of 800 K.W.H. per ton to cover all subsidiary mechanical operations giving a total of 4000 K.W.H. per ton. This represents approximately 160 K.W. per ton zinc per day and is approximately one-third of the energy required by the electro-thermal method. A comparison of the electrolytic figure with that of 23,000 units per ton of aluminium reveals the fact that the consumption of power for zinc is proportionally less.

One of the deterrent circumstances attending electro-chemical industries in this country is that of the assumed high cost of power. From available data it appears that a supply of steam generated current on a scale equivalent to 10 tons of zinc per day (= 1600 K.W.) could be put on the cell house switch board at a cost of ·26d. per unit excluding interest and depreciation and for ·35d. including these charges. On a 20 ton a day plant these figures are reduced to ·24d. and ·32d. respectively. Taking a figure of ·33d. and an energy consumption of 4000 units per ton the electrical costs amount to £5 11s. per ton of cathode metal. This figure would naturally involve every economy including the use of low grade fuel and would be still further reducible on a plant of larger capacity.

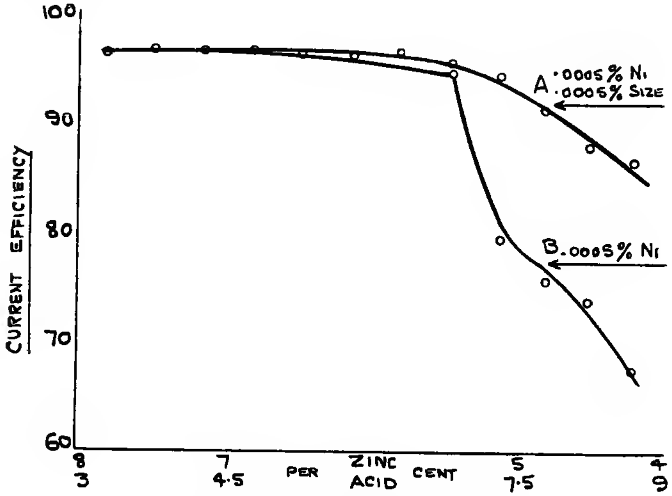

Fig. 6.—Effect of Nickel and Colloid.

Where power might need to be drawn from a large electrical centre the high load factor of the continuous operation provides an incentive for a lower figure per unit than with a smaller and intermittent load.

XIV. Lead and Silver Recovery.

The residues discharged from the filter presses after the crude zinc sulphate solution has been filtered off carry 25 to 35 per cent. moisture, and contain the lead and silver which is now recovered as argentiferous lead. Previous to smelting in a blast furnace, the residues are sintered in a reverberatory furnace. These furnaces may be conveniently built so that the residue is charged in through side doors near to the chimney, rabbled towards the fire-bridge and withdrawn through doors nearest to the fire-place. On a small scale a fuel consumption of about 25 per cent. calculated on the weight of dry residue was incurred.

Two typical assays of sintered residues are given below:—

	No. 1.	No. 2.
Zinc	16 per cent.	12 per cent.
Lead	10 "	20 "
Silver	20 ozs.	10 ozs.

No. 1 is from an Australian concentrate containing:—

Zinc	47·0 per cent.	after extracting 85 per cent. of the zinc.
Lead	6·0 "	
Silver	12 ozs.	

while No. 2 is from a Newton Stewart concentrate containing:—

Zinc	40 per cent.	after extracting 85 per cent. of the zinc.
Lead	10 "	
Silver	5 ozs.	

100 tons of Australian concentrates would leave 60 tons of residues (dry weight) while 100 tons of Newton Stewart concentrate yield 70 tons of residue.

After sintering, the residue is mixed wth the necessary fluxes and charged into the blast furnace with alternate layers of coke. The fluxes required are iron oxide and limestone in the following approximate proportions:—

Residue	51 per cent.
Iron oxide	16 "
Limestone	14 "
Coke	19 "

The recovery of lead and silver is about 85 per cent. A high percentage of zinc in the residue yields a pasty slag holding up lead and silver unless a high temperature is used. A saving of fuel can be effected by the addition of a proportion of high grade galena where available to the residues.

XV. Operating Costs.

It is impossible to give an exact figure for working costs, some of which must necessarily be dependent upon local conditions. A 10 ton a day plant would require 80 employees of which 40 per cent. would be women. This estimate assumes three 8 hour shifts per day. With an average wage of 10s. per shift and a power cost in this country of ·34d. per unit the costs should not exceed the following figures:—

	Per Ton of Zinc.		
Calcination	£3	0	0
Power	5	11	0
Reagents	3	0	0
Melting cathodes	1	10	0
Stores	1	0	0
Salaries and wages	4	10	0
Interest and depreciation	3	0	0
Total	£21	11	0

Interest and depreciation is reckoned at 10 per cent. on the cost of the plant exclusive of electric power plant. One great advantage of the process, however, is the simultaneous recovery of other values such as sulphuric acid, lead, silver, and copper. These by-products should thus bear a proportion of some of the costs including calcination. With a concentrate of 40 per cent. zinc, 10 per cent. lead, and 5 ozs. silver delivered at £5 per ton and the selling prices of pure zinc at £36, lead at £24, acid at £5, per ton and silver at 3s. 6d. per oz., a gross profit of £12 per ton of zinc can be shown giving an annual gross profit of £42,000 on a 10 ton plant. It may be added that the costs above outlined are based on the three-stage purification scheme, and we have confidence that these figures, especially when operating on a larger scale, could be appreciably reduced. A more exact estimate of all costs could better be given when those of raw materials and labour charges have become more stabilised.

XVI. ACKNOWLEDGMENTS.

It may well be assumed, when it is stated that this paper contains but a small fraction of the data and observations which have accumulated during this investigation, that the work did not by any means constitute an individual effort. Briefly but nevertheless fully appreciatively it must be recorded that at all times those entrusted with the task of carrying on the research exhibited from the first an enthusiasm which augured well for ultimate success.

The whole of the research has been financed by the British Metals Extraction Co., Ltd., the directors of which displayed throughout indomitable courage and generous liberality in carrying on in face of the very adverse conditions ruling during the war period. The association of this Company with the distillation industry through the well-known "Villiers' Spelter" placed them in a position in which the scope and comparative values of the two processes distillation and electrolytic could be correctly gauged.

Trying indeed were the times when every effort had to be made and maintained in order to take a place in the waiting queue duly armed with the needful P. certificate to obtain plant to carry on the development of a process which it is believed will secure to the country a large supply of an A1 essential raw material of many industries from otherwise unusable C3 materials.

In the earlier stages the research benefited much by the active co-operation of Mr. H. Livingstone Sulman, Past-President of the Institution of Mining and Metallurgy. The difficulties at first encountered were only overcome after much exhaustive research work in which his initiation and collaboration were of inestimable value. The laboratory experimental work has in part been carried out in the electro-chemical laboratory of the Northampton Polytechnic Institute, London, E.C. 1, by permission of and with the appreciated helpful advice from the Principal, Dr. R. Mullineux Walmsley. The larger scale operations have been carried on in the interest of the Metals Extraction Corporation on a plant with a capacity of 1½ tons of zinc per day at the Llansamlet works of the British Metals Extraction Co., Ltd. Acknowledgment is also made of the services rendered by Mr. Trevor Morgan Williams in the analysis of extensively accumulated data and in the checking of the selection utilised in the paper.

It is hoped that, as a war development, the advantages of which should now accrue to the development of industries of reconstruction, the work will be regarded as of more than merely experimental importance, and that it may constitute a contribution to our effort to raise the present very depressed yet important industry to a level much more commensurate with its association with other important industries, by utilising home resources of low grade and complex ores for the recovery of every value which under scientific treatment will add to the wealth of the country and thus advance its position in the industry and commerce of the world.

DISCUSSION.

Mr. W. R. Cooper said he was very glad the Society had obtained this paper. Many papers which they received were rather on the theoretical side, but the present one was thoroughly practical. Some of the facts discussed by the author had already been mentioned in other papers, but in nothing like the same detail, and they had not been brought out in the same interesting and logical way. In regard to cheap fuel, it did not necessarily follow that from a cheap, low-grade fuel they could get very cheap power: otherwise there would be a brisk demand for such fuel and it would no longer be cheap. There was one point he would like to put to the author; it looked as if the electrolytic process could be applied very well to certain ores in this country, but he gathered that the quantity of these ores available was not very great. If, therefore, the process had to be applied to concentrates imported from Broken Hill, it seemed to him we might be working in the wrong direction. Obviously, the charge for freight would be less for a ton of zinc than for the concentrates from which the zinc is produced, and if the electrolytic process was already being employed to any extent at Broken Hill (which appeared the most suitable location), would it be possible to compete against it in this country after shipping the concentrates here? It would be well if the author could give a little more information on that aspect of the subject.

Capt. S. C. Bullock, M.I.M.M.: I should like in the first place to congratulate the author on his most valuable contribution to the literature on the electrometallurgy of zinc. The paper should be read by all interested in the production of zinc in this country, to whose attention I would draw the remarks made by E. P. Mathewson, Chairman at a recent meeting in New York of the American Institute of Mining and Metallurgical Engineers. He expressed the view that the work of Tainton and Pring at Martinez, California, is the final evidence that furnace methods for zinc production are doomed to extinction. Their experiments show that a small electrolytic plant can be erected having a large output, and it is only where natural gas is extraordinarily cheap and electricity correspondingly dear, that retort smelting can show advantages in costs per lb. of zinc.

Mr. Field has referred to some of the electrolytic plants already in operation elsewhere, and perhaps it will not be out of place if I briefly describe two methods of treatment, with a view to promoting a discussion as to their respective merits, compared with the process outlined in the paper now before us.

The Anaconda Company of Montana was the first to put into commission in November, 1915, a 10-ton plant, shortly afterwards erecting their present plant at Great Falls, which commenced operations in September, 1916, and is now producing over 150 tons per day.

The Anaconda Process is, with certain modifications, the method adopted in America and Australia for the production of zinc by electrolysis.

The concentrate is roasted in the usual manner, Wedge furnaces being used, leached in a weak acid solution and subsequently releached in a much stronger acid solution. This method is called the neutral plus acid leach, owing to the solution being completely neutralised in the first stage but remains still slightly acid after the second stage, and it necessitates a series of filtering operations.

Purification is comparatively simple as nickel and cobalt are absent. A large amount of zinc dust, however, is used for precipitating copper and cadmium, about 8 per cent. of the cathode zinc produced, being used for this purpose at the Anaconda Plant.

In the cell system a combination of the cascade and individual feed is used to regulate the acidity of the solution.

The main difference between the Anaconda Process and that described by the author is that the former uses air-agitation and cold solutions whilst the latter makes use of mechanical agitation and hot solutions. The latter method undoubtedly ensures a more perfect purification with its consequent advantages.

The other plants mentioned by Mr. Field, *i.e.*, Trail, Judge, Risdon, are very similar in operation and design to that at Anaconda.

There is one experimental plant now working on a 1 ton per day scale at Martinez, California, using the Tainton and Pring Process. Here a very high current density—100 amperes per sq. foot—and high acidity are used necessitating very elaborate methods of cooling for the cells. The power used is correspondingly high, the ratio of zinc produced at present by the three different methods of treatment being approximately as follows per horse-power day:—

B.M.E. 12 lbs. of zinc; Anaconda 11 lbs. of zinc; Martinez 10 lbs. of zinc.

Since the consumption of power is the principal item in the cost of production, the process producing the greatest quantity of marketable zinc, other conditions being equal, for a given amount of power will be the most successful.

Mr. H. M. Ridge said that whilst he would like to add a word of congratulation to the author, he was afraid at the same time he must put forward some criticism. His own first experience of electrolytic zinc deposition went back to 1896 or 1897 and since then he had repeatedly been faced with the problem of electrolysis versus fire distillation. He had always had a predeliction in favour of the electrolytic method where he could possibly adopt it, but in the past he had always been forced to the opposite conclusion, and if Mr. Field could persuade him of the error of his ways, he would be extremely pleased to follow him. For the title of the paper, he would have preferred to see it called "The Electrolytic Treatment of Zinc Ores," but that was a small point.

The paper quoted figures of the home consumption of zinc, but it did not sufficiently state the case. The position was far more acute, and that point should be emphasised for the benefit of the legislators and also the British public, because the more zinc and zinc products we were able to make in the country, the less we should have to import. Products of great importance such as zinc dust, zinc oxide, lithopone, etc., never appeared in the figures quoted, and they did not come into this paper, although they were important articles of commerce. The British ore supplies were much more important than might be imagined from a perusal of the Board of Trade returns. He believed he was right in saying that at the present moment the production of British zinc ores had entirely stopped because they could not pay their way.

With regard to the Government contract for Australian zinc concentrates which the author mentioned, the tonnage went up to 300,000 per annum, but at present there was not the slightest hope of our being able to treat any appreciable proportion of them in this country. Apart from the fact that the whole of the South Wales zinc smelters had shut down, there were now only two plants working in this country, and in one case he had been told the works were carrying on uncommercially, in order to keep the staff and men together. The other works had been going on satisfactorily, but were short of ore. The position was disastrous, and zinc smelting in this country was apparently coming to a rapid end unless conditions altered materially. The only thing that would go on, presumably, was the treatment of a certain amount of zinc residuals, but under present conditions, prices, and freights, it was impossible to import ore with spelter at £23 or £25 and to pay the mine a price at which it could live; that applied to both electrolytic and fire distillation methods. It was true that neither the Belgians nor the Americans could produce metal at a profit and there was only one country in the world that could, *viz.*, Germany, and that was due to the depreciated exchange. As a result, Germany had knocked the bottom out of the market over here, at any rate for the time being. How long that would last was uncertain, but, coupled with the extraordinarily low consumption, the world's production must continue for a period to be small.

He could not agree with the author's use of the word "calcination". This is in general use in the Duchy of Cornwall, but the use is incorrect. The de-sulphurisation of zinc ore could not be carried out by calcination; it was a roasting operation pure and simple, and there was a distinct difference between the two.

He would like to ask the author with regard to cadmium, whether it was not possible, after the harmful elements such as nickel, cobalt, etc., had been removed, to eliminate the cadmium by differential electrolysis. There were certain indications pointing to that possibility, and it appeared worthy of consideration.

The question of costs was the prime essence of the whole business. In England, before the war, we were faced with power costs approximately double what had to be paid in Scandinavia. The lowest price quoted to him for a bulk supply in Great Britain was 85s. per H.P-year. That was some years before the war, but at the same time power was offered in Scandinavia at less than half that price so that the electrolytic treatment of zinc ores could not flourish in this country, but would gravitate to Scandinavia or parts of Canada where there were enormous water powers, in Ontario and British Columbia. It would also extend to Tasmania, where the available water power was limited but cheap. The H.P-year cost about £8 here now compared with which the Electrolytic Zinc Company of Australia was paying the Tasmanian Government 40s. or 45s. At the same time, he had to disagree with the author's working expenses. It was stated in the paper that some time ago the working expenses were in the ratio of £30 for distillation to £20 for electrolysis. As a matter of fact he had been producing spelter in this country by the distillation process at a lower figure than that mentioned, but that could only be done in modern plant equipped with labour and coal-saving devices. It was necessary to arrange for a minimum coal consumption for heating the furnaces; they must not consider some of the wasteful old-fashioned furnaces as used even up to last year in the country. In the newer furnaces the coal consumption has been reduced by one half. It was necessary to have the modern plant throughout.

Regarding the contention that the electrolytic method was applicable to low grade ores, might he recall that on the Continent before the war—he did not know what they had been doing since—zinc ores were charged into the retorts for distillation containing as low as 15 to 18 per cent. zinc, and money was not lost; in fact the practice was profitable. The skilled labour question in connection with the distillation process had been largely overcome by the use of machinery, and the author's figure of 70 to 75 per cent. recovery by the distillation process was appreciably too low. The results were much higher than that even with to-day's labour conditions.

The question of high grade metal was distinctly important. During the war, we were faced with a shortage of high grade zinc for cartridge brass, etc., but in the same manner that our countrymen had tackled other difficult problems, so the problem of high grade zinc had been tackled, and it should be a source of pride to the whole of the metallurgists in the country that to-day we were able in England to make high grade zinc economically and cheaply by fire methods. The Ministry of Munitions found this metal as good or better than that made by the electrolytic process and it was much cheaper. That was a source of congratulation, because it was a new method evolved in England and it worked entirely satisfactorily and gave excellent results.

Regarding electrolysis in Great Britain, several plants had been built and worked. The best known of them was the Hoepfner process of Brunner Mond, which, he believed, produced the purest zinc ever made in the world by electrolysis. The quality was good, but the plant was started originally in order to obtain pure chlorine. Since those days, cheaper methods of producing chlorine had been devised and were in commercial use, and there was not the same necessity for the Hoepfner process. Enormous difficulties had to be overcome initially before that plant worked properly. These difficulties were overcome satisfactorily, but owing to altered conditions of trade the plant was shut down very soon after the armistice and had since been dismantled. That plant, he believed, was the only electrolytic zinc chloride plant in the world; he did not know of any other himself, except experimental ones. There had been quite a series of electrolytic plants built in this country for sulphate solutions. Before the war there was a plant on the Tyne, and in later days during the war there were plants built at Widnes and Oldbury. Unfortunately none of them were any longer in existence, but he hoped that the company with which Mr. Field was associated would be more successful. There always remained the difficulty in Great Britain, however, of high power costs.

Mr. D. F. Campbell thought Mr. Ridge was unduly pessimistic with regard to the future of electrolytic zinc. In the first place, the mere fact that the productive capacity of electrolytic zinc works in the world to-day was equal to about 10 per cent. of the total productive capacity of the world, was sufficient evidence that electrolytic zinc must have a future. It was true that the majority of the works were idle to-day, but that was due to trade conditions, and the fact that it was impossible to produce zinc at £26 per ton was no proof that the electrolytic process was not satisfactory.

The object of the discussion should be to arrive at a relative value of the old retort process as compared with the new electrolytic process.

That was the first question, but whether the new process could be made commercially successful in England was another matter which might possibly be doubtful. There was no doubt whatever that the industry could be established in the British Empire on a very large scale. The conditions in Tasmania were essentially good. The price of power to be delivered by the Government hydro-electric station was 40s. per E.H.P.-year with a possible increase to 50s. if the zinc works were very profitable, the price of power increasing according to the profits subject to a basic price of 40s. per E.H.P.-year. On the other hand, the amount of power used was comparatively small: 4000 units per ton was not a large amount compared with ferro-chrome which used 7000 to 8000 units per ton, aluminium which used 20,000 to 30,000 units, artificial graphite which used 11,000 units, and carbide 3000 to 4000 units per ton. He thought it could be stated that zinc was one of the industries which could be established with power at a moderate price. It was not like carbide of calcium, which was very cheap and required low priced power, or aluminium, which required an enormous amount of power. In the case of each of these products, power was one of the principal items in the cost of manufacture. Therefore, zinc by electrolytic treatment of the ores could be considered a process that could afford topay a moderate price for power. As to the establishment of industries in Norway, there were serious disadvantages at the present time in going to Scandinavia; there were the questions of taxation, concessions, and Government difficulties, and the mere fact that it is legally necessary to have in the works Norwegian workmen, managers and staff was a very strong reason for keeping within the British Empire.

There was one other point about the cost of power in this country to which he would like to refer. He thought the author's estimate of ·33d. or ·35d. per unit as the cost of power generated in England for such a process was optimistic, but not impossible of achievement. There was a 95 per cent. load factor, and on a large system they had the possibility of giving a leading power factor, which was a great advantage to the power company, and for that reason a cheaper price should be possible. The cost of generating power with gas from coke ovens or waste products from collieries before the war was about ·33d. It was actually done at that price on a very large scale until about 1917, but the whole question depended on the price of coal. It must not, however, be assumed that large quantities of valuable coal dust will be available at normal costs as the value of every calorie available is becoming well appreciated. In generating power both load factor and power factor were very important, and the electrolytic process of zinc production was ideal from the point of view of the power company, because both factors were in their favour. In the comparison of this process with the old process it must be remembered that 5 tons of coal at least was required to produce a ton of zinc with the old process, and the relative merits of the electrolytic process as compared with the old process depended very much on the future price of coal.

The difficulty of getting labour to stand the arduous and disagreeable work of attending to zinc retort furnaces was also a factor, which should favour the electrolytic process, especially in Great Britain, Australia, Canada, and other countries where the amelioration of working conditions is receiving so much consideration.

Dr. J. N. Pring (*Communicated*): With reference to the data plotted in Figs. 4 to 6, it would be of value if Mr. Field would state the current densities employed under the different conditions. It was found by Mr. Tainton and myself[1] that the possibility of obtaining coherent deposits from solutions with high-acid concentrations is associated with the use of high current densities. In a process now in commercial operation, the current is taken as high as 500 amps. per sq. foot of cathode while the acid concentration may amount to 20 grms. per 100 c.c. It is found possible to employ incompletely purified solutions by adjusting the conditions of the electrolysis. The presence of small quantities of colloidal matter leads to increased smoothness of the deposited metal and modifies considerably the conditions of operation.

Mr. T. Wallace (*Communicated*): In 1916 I had some experience in running a small electrolytic zinc plant making a ton per day by much the same process described by Mr. Field, and there are one or two points in his paper which seem to call for comment.

The author remarks that the electrolysis is effected between lead anodes which are exceedingly permanent under normal care.

Comment on this statement would have been easier if some idea of the life of the anodes had been given. My experience was that the lead anodes were far from permanent and were often a source of considerable trouble. The lead was steadily converted into lead peroxide, which, occuping more volume than the lead, caused the anodes to buckle severely, and often caused short circuits by lumps of peroxide falling over on to the cathodes. At the end of about six weeks it was usually necessary to change the anodes. In fact there was a regular routine of anode changing based on about six weeks' life. At the end of that time the anode was a heavy buckled sheet of peroxide on a very thin lead centre. The bottom portion had often gone altogether, the peroxide collecting in the bottom of the box.

Another unsatisfactory feature was the difficulty of maintaining a good electrical connection to the anode. Stout copper clips were forced on to a wedge-shaped projection from the top of the anode. These frequently became too hot to touch and had to be removed and cleaned.

On the whole, from my experience I should say that the lead anodes are far from being permanent, and also necessitate constant supervision of the cells to prevent short circuiting and heating of the connections.

I agree with the author that the purification of the liquor is the keystone of the whole process, but my experience differed from his. In 1916 we were not always able to obtain the ore we liked and consequently our experience was varied. The two ores with which I had most to do were Australian Concentrates and Vielle Montagne from Nenthead in Cumberland. With the former we always obtained excellent results, and with the latter we always had trouble. We were troubled with the same kind of corrosion as the author attributes to cobalt. We also experienced in a less degree the kind he attributes to nickel.

I must say here that the presence of these two metals were never suspected. They were two impurities we did not worry about. It is rather peculiar that our results were bad with an ore containing no nickel[2] and good with an ore containing a trace of this impurity. After much trouble from this kind of corrosion we came to the conclusion that the source of the trouble was iron in the ferrous condition.

This conclusion was borne out by our experience, that as soon as we could get regular supplies of solution free from ferrous iron, then we had no trouble. With Australian Concentrate we could always manage this:

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[1] *Trans. Chem. Soc.*, 1914, **105**, 710; Brit. Pat. 7235 of 1911.

[2] See author's analyses.

with Vielle Montagne scarcely ever. The ore was roasted to zinc oxide and treated with acid in much the same way as the author describes. It was never found necessary to add whiting to neutralise the acid. This could always be done with adding ore. In the same vat excess ore was added to precipitate the iron, and the solution was carefully tested with sulphocyanide for ferric and permanganate for ferrous iron before going into the next vat. With Vielle Montagne ore we could never get rid of the ferrous iron in the solution. Attempts to oxidise to ferric iron by blowing in air and stirring with lead peroxide from the cell room were of little use. We never found it possible to completely purify the solution from this impurity. I was struck in the paper by the author's brief mention of iron and his neglect of what, to us, was a vital matter, *viz.*, the question of removing ferrous iron.

After freeing the solution from iron, when possible, and pumping into another vat, a bucket of ferrous sulphate was added to precipitate any arsenic which might be present. Arsenic was always regarded as a very deadly enemy, but I never was troubled with it in the liquor. The final stage in the purification was the stirring with zinc dust to remove copper. Cadmium would also be removed by this process, but we never bothered about it. The solution was always free from copper before being run down.

With Australian Concentrates excellent results were obtained from liquor prepared as I have outlined. Using this ore there was never any difficulty in obtaining liquor quite free from iron. We always found that ferrous iron in our solution meant trouble in the cell room while its removal usually meant the end of our troubles.

The ferrous iron was of course oxidised in the cells and was subsequently easily removed in the ferric state, consequently on changing to Australian Concentrate one passage through the cell room was sufficient to purify the liquor. This question of the effect of the iron was never tested in the laboratory, but our experience in the works seemed to point that it lay at the root of our difficulties.

The ores which gave us trouble with ferrous iron usually gave us trouble in the settling. The liquor obtained in the extraction of the roasted concentrates invariably settled very quickly, and usually the liquor was so clear that it was not necessary to put it through the filter press. With Vielle Montagne ore the settling was always a very slow process. In fact we found that generally speaking we either had an ore which gave us trouble in all sorts of ways or an ore that was no trouble whatever. We found that the addition of solution of glue often had a beneficial effect on the settling of the residue.

Given Australian Concentrates we could obtain a good yield on 99·95 per cent. zinc with ease, but with Vielle Montagne or any ore which gave us ferrous iron in solution the yield fell off considerably. We may have been wrong in ascribing our troubles to ferrous iron, but we certainly had trouble in its presence and success in its absence.

Mr. Ernest A. Smith (*Communicated*): In view of the national importance of an adequate supply of zinc to the United Kingdom both in times of peace and war, and the desirability of increasing the home production of this indispensable metal, the paper by Mr. Field is very opportune. The circumstances arising from war conditions focussed attention on the very unsatisfactory state of zinc production in this country, and emphasised the need for developing the industry so that the quantity of metal produced should be more commensurate with the increasing requirements of industry.

Much has been written in recent years on the production of electrolytic zinc generally, but, as pointed out by Mr. Field, little has been published relative to the application of this method of zinc extraction to the treatment of ores in this country. A considerable amount of experimental work on the electrolytic production of zinc on a commercial scale has been done in America and elsewhere, and the results of this work have doubtless been of considerable assistance to Mr. Field in his investigation. It is to be regretted, therefore, that fuller reference has not been made in the paper to such work.

The results obtained by Mr. Field appear to indicate that given favourable local conditions the electrolytic process has a good future before it, inasmuch as it offers a solution to the vexed question of treating the zinc ores that have long been known to exist in this country, but which have not hitherto been worked to any extent owing partly to their complexity and unsuitability for the usual distillation process of zinc production.

For many years the annual production of zinc ore in the United Kingdom was between 20,000 and 25,000 tons, but during the past decade the output has fallen to about 17,000 tons. It is now well known that in pre-war days a large proportion of the zinc ore mined in this country was, after concentration, shipped to the Continent for smelting, which is a clear indication that under suitable conditions some of the ores could be profitably worked and treated by distillation. Thus out of a total of 17,000 tons of zinc ore mined in the British Isles in 1913 some 13,000 tons was exported mainly to Belgium for treatment.

There is little doubt, however, that if further trials substantiate the results so far obtained the electrolytic process may prove to be the most suitable process for treating home ores, and if this should prove to be the case, it should do much to stimulate the mining of zinc ores in the United Kingdom.

The best known deposits are those in: Flintshire, Cardiganshire, Durham, Cumberland, Derbyshire, the Isle of Man, Dumfriesshire, and Lanarkshire.

Attention is now being directed to the possibility of developing these and other sources of zinc ore in the country which, by the application of modern methods of concentration, and adequate financial support, may yet prove to be a valuable national asset.

The question of ore supply is one of fundamental importance, and has been met to some extent by the arrangement between the British and Australian Governments for the importation of the well-known Broken Hill Concentrates which contain on an average about 46·5 per cent. of zinc. To what extent this supply of raw material can be augmented by ore mined in this country remains to be seen.

In establishing a new process locality is also a question of considerable importance, and it is gratifying to learn that Swansea, which has so long been associated with British non-ferrous metallurgy, is proving a suitable centre for establishing an electrolytic zinc industry.

Mr. Field has done well to point out that "the success of any electrolytic process, will always need to be judged by its adaptation to local conditions". The success of the electrolytic zinc process at Anaconda is frequently quoted in support of its introduction in other districts, but it is necessary to remember that the conditions at Anaconda are exceptional. The ore, which is mined as a secondary product in copper ore mining, is of a special nature and not only lends itself very successfully to treatment by the flotation process, giving a high grade zinc concentrate, but it is also so amenable to roasting and leaching with dilute sulphuric acid that the greater part of the zinc is easily obtained in the form of sulphate solution.

In recent years there has been a growing demand for zinc of high grade quality for rolling and alloying purposes, so that a ready market should be obtained for the electrolytic zinc produced. The rolling of electrolytic zinc into sheets requires a slight modification of the ordinary method of rolling as applied to commercial spelter, and rather more experience, but the sheets produced possess enhanced properties, especially for building purposes. Further work with a view to the establishment of an electrolytic zinc industry on a satisfactory basis in this country will be followed with considerable interest.

A very useful comparison of the plant required for the extraction of zinc by the distillation and electrolytic processes has been given by Mr. Gilbert Rigg in the "Report on Zinc" (1913 to 1919) recently issued by the Imperial Mineral Resources Bureau.

He points out that "for a production of 100 tons of spelter per day from Broken Hill roasted concentrates by the distillation process we should require a furnace plant of 9000 retorts of 1·5 cubic feet capacity each, which at 300 retorts per furnace would mean thirty furnaces with a producer plant to gasify 225 tons coal per day.

For a similar production by the electrolytic process we should require a power installation of 22,500 horse-power together with leaching equipment to deal with 225 tons roasted ore per day and electrolytic cell plant to deposit 100 tons metal daily.

This comparison will serve to indicate in a very general way the relative size and shape of the two plants.

In three respects the electrolytic process has a distinct advantage over the distillation, namely: (1) more complete recovery of the zinc, (2) less demand on the operatives, (3) the purity of the metal which is independent of the purity of the ore.

Mr. S. Field (*Communicated reply*): The discussion has served to bring out some further points associated with electrolytic zinc which were omitted from the paper, mainly owing to considerations of space. For example, Captain Bullock has referred to the salient features of the several processes now in operation in other countries, thus showing how firmly the industry is taking root in localities peculiarly circumstanced by reason of comparatively pure ores and cheap power. Reference is there made to the process of Tainton and Pring at Martinez, and it would have been of interest had Dr. Pring, in his communication, stated the consumption of power in his process employing so high a current density. A comparison with our figure of 3200 K.W.H. per ton of cathodes might have proved instructive.

Our experience of impurities differs somewhat—even considerably—from that of Mr. Wallace. This difficulty of the rapid disintegration of the lead anodes by peroxidation was, for a time, experienced, but subsequently entirely surmounted. The lead anodes should become superficially peroxidised and the lead peroxide act as a protective film. We are convinced that lead anodes, used under the best conditions, are very serviceable and cheap. There should be no need for anode changing at so short an interval as that mentioned by Mr. Wallace.

With reference to iron in the zinc liquors, there can be no doubt that in small amount it lowers current efficiency. Our only brief mention was due to the fact that we had no difficulty in reducing the iron to a harmless amount by the process mentioned. Iron in our ingots never exceeded ·01 per cent. Cadmium is, we believe by experience, more difficult of removal. Its electro-chemical properties indicate this. It is not so readily removed as may at first be imagined. Traces of cadmium need careful looking for. Practically all the cadmium left in the solution passes into the deposit. On account of induced brittleness, readily observed in the cathode deposits, it is very undesirable. From every point of view pure solutions must constitute the golden rule of electrolytic zinc.

Mr. E. A. Smith makes some timely remarks on the subject of electrolytic zinc prospects in Great Britain. He will, however, be aware of the very scanty reference in the technical press to anything which really counts in modern electrolytic zinc work which appeared before substantial progress had been made with the work in 1916. There can be no doubt that in this country there are large bodies of ores unsuited to distillation, but upon which the electrolyte process could be profitably applied. Illustrations have been given. Others are from time to time coming to light. We are optimistic that the near future will give a commercial demonstration of the fact. The application of the process upon home ores will at once be beneficial to the mining industry, a resuscitation of which would at least be desirable in these days of unemployment and industrial depression. The advantages of the treatment of home ores in preference to being dependent upon metal imported from distant localities like Tasmania are, we think, sufficiently obvious to constitute a reply to Mr. Cooper's query on this point. The subject of power has been raised by several speakers. Although power is an important item it by no means fills the bill of costs. Moreover, it is certain that the attention which is now being paid to the utilisation of low grade coals for steam raising will point the way to power of a sufficiently low order of cost to justify increased electro-chemical activity in this country. The comparatively low cost of low grade fuel combined with the high load factor at least indicate that processes of moderate power consumption—for example electrolytic zinc—should not fail on account of suitably priced power. It is gratifying to find that Mr. Campbell agrees with this view.

Mr. Ridge raises a number of points capable of a simple reply. His predeliction will doubtless be soon followed by conversion to electrolytic zinc. There are no special circumstances attaching to any electrolytic zinc-producing country which cannot be proportionately and commercially reproduced here. The zinc depression of 1921 should at least direct special attention to the subject. Water power is not a sole determining point, and a ratio of double the power cost in Great Britain over that of Scandinavia would not necessarily involve a gravitation of the industry to that country. Moreover, Mr. Ridge would surely agree that no zinc industry could possibly be based on the retorting of a 15 to 18 per cent. zinc ore. The introduction of mechanical appliances in the zinc industry is by no means universal, and it is doubtful whether such additional capital outlay could now be incurred in an industry faced with such heavy charges and almost certain extinction. The removal of cadmium by differential electrolysis is difficult, and, fortunately, unnecessary. Purification by the methods described is effective in reducing cadmium down to ·02 per cent. and less in the final product.

We find it necessary, however, to pause before too readily accepting the statement with reference to the production of high grade zinc by fire methods as a commercial competitor of electrolysis. Taken altogether, the prospects of a British electrolytic zinc industry were never more promising than they are to-day.

THE FORMS OF ELECTRO-DEPOSITED IRON AND THE EFFECT OF ACID UPON ITS STRUCTURE.

PART I. DEPOSITS FROM THE CHLORIDE BATH.

By W. E. Hughes, B.A. (Camb.).

(*A paper read before* The Faraday Society, *Tuesday*, *March*, *22nd*, 1921, Professor Alfred W. Porter, F.R.S., President, *in the Chair.*)

Introduction.

During the last three years the author has been able to examine with the microscope a large number of samples of electro-deposited iron. The variety of structure shown by the metal upon such examination was so great that there seemed, at first, but little chance of reducing the chaos to ordered classification of forms. It is, however, known that in the consolidation of deposited metal one has to do with a crystallisation process,[1] and it is also known that the result of that process—the crystal grains—depend for their size and shape upon the conditions under which they are formed. A search was, therefore, made through the literature to ascertain whether anything relating to deposited metal could be found that would be helpful. This search disclosed that there was very little information contained in the literature of electro-metallurgy that threw light upon any association between the structure and conditions of formation of coherent and crystalline deposited metal; but some work published by A. Sieverts and W. Wippelmann,[2] in 1915, upon the structure of electro-deposited copper, as also a paper published by O. Faust[3] upon the structure of the same metal, showed that there is, in the case of copper, a definite relationship between structure and conditions of formation. As a consequence, a series of experiments was carried out with the object of establishing, if possible, the various sets of conditions of deposition that would lead to this or that form of structure of deposited iron. The results obtained were encouraging: they are embodied in a report made upon electro-deposited iron to the Scientific and Industrial Research Department. Examination of still other samples of the deposited metal, formed under known conditions, confirmed these results; and the author was fortunate enough to find among the samples examined during this later work one that contained in itself many, if not, perhaps, all, the different forms of structure that had been previously observed in the individual specimens. This deposit is, therefore, interesting in that it can be looked upon as an epitome of many others; and it is of added interest for the reason that in it is very clearly shown the effect of the presence of acid in the electrolyte upon the structure of the deposited iron—a matter not particularly considered by the author elsewhere. It may be remarked that the deposit was formed in the chloride bath, as is described below: the present communication has reference to the structure of such deposits only.

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[1] *Cf.* F. Foerster, *Elektrochemie wässeriger Lösungen*, 1915, p. 328.

[2] *Zeit. anorg. Ch.*, 1915, Vol. 91, p. 1.

[3] *Ibid.*, 1912, Vol. 78, p. 201.

DEPOSITION.

The solution employed was composed of ferric chloride and calcium chloride, dissolved in water. Ferric chloride was used as no ferrous salt was available. It was necessary, therefore, to first reduce the ferric iron to the ferrous state, and this was done by adding HCl to the solution and passing a heavy current through the bath between sheet-iron electrodes. The course of the reduction was checked by testing for ferric iron with the usual reagents.

Before describing the formation of the deposit that is, in particular, the subject of this communication, five deposits which were formed under the conditions given in Table I. will be considered. These deposits are referred to here, because they confirm, in several respects, work previously done on the ferrous calcium chloride bath,[1] and, further, they show the effect of the presence of acid in the depositing solution upon the macroscopic appearance of deposited iron.

A. EXPERIMENTS ON THE EFFECT OF ACIDITY.

The solution consisted, in the first instance, of:—

$FeCl_3$ solution . . sp. gr. = 1·375 (56 per cent. $FeCl_3$),
and $CaCl_2$ anhyd. . . lbs. 5

The volume of the solution was 3 gals., and it was contained in a rectangular wrought-iron tank, lined with asbestos board. The anodes were $\frac{1}{16}$ in. steel sheet (9 ins. × 6 ins.). The cathode was, in each experiment, a short length ($1\frac{3}{4}$ in.) of solid copper rod, highly polished and carefully cleaned. The acidity of the solution, after reduction of the ferric iron to the ferrous condition, was such as to turn red Congo paper to a grey-blue colour.[2]

Conclusions from Experiments 1 *to* 5.

1. Very slight acidity results in a deposit that is either matt or very minutely crystalline. The aspect of the deposit usually changes, if the period of deposition is considerable, from dull matt to minutely crystalline.
2. A deposit formed in a *slightly* acid is somewhat malleable (Nos. 1 to 4).
3. Considerable acidity causes the deposit to be bright and, to the eye, non-crystalline (No. 5).
4. Considerable acidity causes the deposit to be hard (*cp.* Nos. 1 to 4 with No. 5).
5. Once the bath is acid, considerable time is necessary to effect neutralisation by means of passage of current (Nos. 1 to 4).

The Effect of Acidity upon the macroscopic aspect of the deposit is, therefore, to reduce the size of the grains of which it is composed.[3] The following series of changes of aspect is noted as the solution changes in reaction from acid to neutral:—

Bright, and, apparently, non-crystalline → dull matt, and, apparently, non-crystalline → dull, but minutely crystalline → glittering and crystalline → coarsely crystalline.

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[1] Sometimes known as the Fisher and Langbein bath. D.R.P., No. 212,994 (1908); D.R.P., No. 228,893 (1909); D.R.P., No. 230,876 (1910).

[2] It was considered superfluous to use solutions of known strength in acid. For present purposes colour comparisons of Congo paper appear quite sufficient.

[3] *Cf.* Sieverts and Wippelmann, op. cit.; and for the effect of acid in the Bett's lead refining solution, *v.* W. D. Bancroft, *Trans. Am. Electroch. Soc.*, 1912, Vol. 21, p. 233.

TABLE I.

No. of Expt.	C.D., Amp./Ft.^{2}	E.M.F. Volt.	Temp. °C.	Time, Hr.	Deposit.	Remarks.
1	140	—	95	3	Very good. Light grey. Matt. Malleable.	*Acidity.*—Congo paper turned grey-blue.
2	140	—	95	3	Good. Light grey. Crystalline—crystals minute. The outgrowth at the bottom end was rounded.	*Acidity.*—Congo paper changed only very slightly—to a light slate colour. But there was still sufficient acid to act upon the anodes even when no current was passing.
3	140	1·6	97	2½	Good. Light grey. Matt, and plastic in appearance as No. 1. Malleable.	*Acidity.*—Still sufficient to turn Congo paper to a slate grey colour.
4	140	1·6	95	4	Good. Light grey. Crystalline—crystals minute. Rounded outgrowth at lower end. A little harder, perhaps.	*Acidity.*—Only sufficient to very faintly affect Congo paper. The acidity was evidently less than in No. 3.
5	140	—	95	4	*At first*, before acid addition, light grey and crystalline. *Then*, after acid addition, light grey. Bright and, to the eye, non-crystalline. Very hard.	*Acidity.*—Sufficient HCl was added, after deposition had proceeded for a while, to turn blue litmus to a bright red and Congo to a dark blue.

B. Conditions of Formation of the Principal Deposit.

The bath used for the experiments 1 to 5 was made so acid that Congo paper was turned to a deep blue-black colour. Two new anodes of sheet iron were employed. The deposit itself is compound, each part being formed during a separate period of deposition, and the two parts being joined by a thin layer of copper. The general details of the electrolysis were as follows:—

1st Period.

Cathode Copper rod (as in Nos. 1 to 5).
C.D. 140 amp./ft.^{2}.
E.M.F. (*volt*) 0·7 (electrode distance = 3½ ins.) at the beginning, but this increased as the electrolysis proceeded.
Temp. 100° C.
Time 7 hours.

2nd Period.

Conditions same as in 1st period, except—
Time 2¼ hours.

Details of the Course of the Electrolysis During the First Period.

Time, 4 hours.—One effect of the presence of free acid in the bath was a copious evolution of hydrogen at the cathode. A consequence of this is that the observer can note (roughly) the diminution of free acid content from the lessening of the volume of hydrogen evolution. Using this fact as criterion, the acidity was observed to diminish somewhat rapidly during the initial period of deposition, and then more slowly. HCl solution (1 : 10) was added from time to time in quantities (1 to 2 c.c.) just sufficient to maintain the solution acid. It was noticed, here again, that upon each addition of acid the deposit became more hard and metallic in appearance, and closer in grain, and that *as the effect of the acid diminished* (*i.e.* the bath became less and less acid), *so the deposit gradually changed from metallic and bright to matt and reguline, and finally became minutely crystalline.*

Time, 1⅓ hour.—During this period the additions of acid were discontinued. As a consequence the bath had, at the end of 5 hours' deposition, come to contain very little, if any, free acid. This resulted in some oxidation of the solution, marked by the formation of a skin of oxide on its surface.

Time, 1⅔ hour.—10 c.c. diluted acid (HCl) were added. The deposit —crystalline before the addition—gradually (but rather quickly) attained the hard and metallic appearance again, and its colour changed from light grey to dark and bluish. At the same time, some outgrowth that had formed round the bottom edge of the cathode changed from a cindery to a rounded form.

At the end of the period the deposit had recovered its light grey and matt appearance, but it did not appear crystalline at all to the naked eye.

The cathode was then removed from the bath.

Details of the Course of the Electrolysis during the Second Period.

The cathode was removed from the potash solution in which it had been placed in order to prevent it rusting overnight, and the outgrowth round the bottom edge knocked off or flattened down. It was then cleaned in an electric cleaner, suspended in the cyanide of copper tank for two minutes, in order to form a slight coat of copper upon the iron deposit, swilled through water, diluted HCl, and, again, water, and then returned to the depositing (iron) bath. The solution was made just sufficiently acid to react to Congo paper, and the electrolysis was allowed to proceed without interference, except that the cathode was occasionally removed for the purpose of inspecting it. At the end of the period (2¼ hours) the deposit possessed the following characteristics: Light grey colour; very obviously crystalline—it was lustrous and sparkling after being washed and dried; so malleable that when struck with a hammer the deposit was easily flattened out. The thickness was 1·5 mm. (approximately), and was uniform all round the annulus.

MICROSTRUCTURE.

Fig. 1 shows a polished and etched cross-section of the deposit. In the first place, it will be noted that the two periods of deposition are separated by a black line—the locus in the specimen of the thin film of copper formed upon the iron deposit of the first period. It is very noticeable that the copper cathode on which the deposit was formed has not etched at all. A like remark applies to the thin layer of copper deposited upon the iron deposit of the first period and seen at high magnification in Fig. 2. The copper (rod) base will serve as a starting place for description.

The structure of the iron deposit near the cathode (copper) is clearly of a fibrous type: it continues to be so as far as A (Fig. 1). In this section the only noticeable variation of the structure is the widening of the fibres in places, as, for instance and especially, at B. In the section C there is a continuous broadening of the fibres from within outwards so that the grains lose entirely their fibrous form, and the deposit becomes of the normal type. At D_1 a complete change of structure occurs. The deposit between D_1 and D_2 can scarcely be seen (at the magnification of the photograph) to have a structure at all, except towards the outer edge of the band where the apparently structureless deposit merges into metal possessing a distinctly fibrous structure. From D_2 to the thin copper (the dark line in the photograph) the structure remains fibrous, though as the copper layer is approached the fibres broaden somewhat.

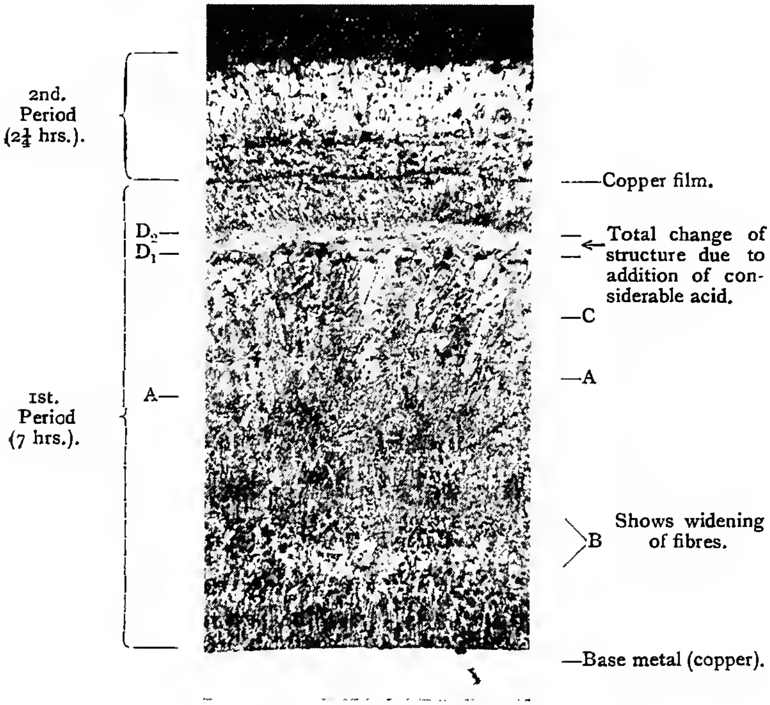
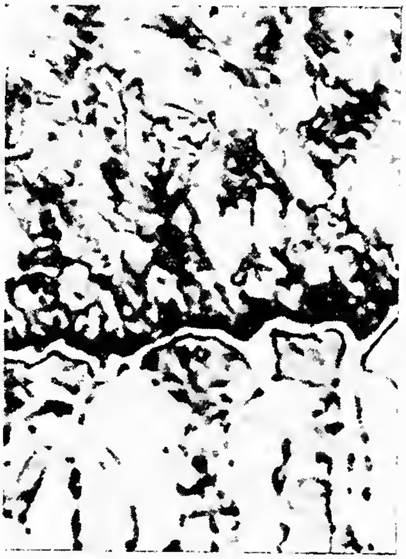

2nd. Period (2¼ hrs.).
1st. Period (7 hrs.).
D₂—
D₁—
A—
—Copper film.
—Total change of structure due to addition of considerable acid.
—C
—A
B Shows widening of fibres.
—Base metal (copper).

FIG. 1. × 60.

The section of the deposit above the copper layer is the part formed during the second period of deposition. It is obviously fibrous within and gradually becomes coarser and more open as the periphery is approached. Some circumferential lines are noticeable in this section. It may be said at once that most, at any rate, are due to removal of the cathode from the bath for inspection purposes: the lines indicate, therefore, breaks in the continuity of the deposition.

CORRELATION OF CONDITIONS OF DEPOSITION AND STRUCTURE.

If the observations made upon the changes in the appearance of the deposit during its formation be borne in mind when studying the structure of the deposit as shown in Fig. 1, it becomes clear that a number of definite conclusions can be drawn with respect to (1) the relation between macroscopic and microscopic features, and (2) the effect of the conditions of deposition of the metal upon its structure—in the particular instance the effect of acidity.



Shows the thin un-etched copper film.
FIG. 2 × 3000.

(1) *Relation Between Macroscopic and Microscopic Features.*

Briefly, it can be said that the connection between these features is so close that an operator can form an opinion as to the internal structure of a deposit as a result of his periodical inspection of the exterior. For instance:—

(*a*) A very close-grained, matt, and, so far as the unaided eye can see, non-crystalline exterior connotes a fibrous interior; while

(*b*) A crystalline external appearance is the mark of a coarse grained internal structure—one that approaches more or less closely to the normal type.

(*c*) A bright metallic appearance indicates that the internal structure is of such fine grain that it is visible at higher magnification only.

A knowledge of these relations between macroscopic and microscopic features is of great importance in connection with the proper control of the deposition of iron in the workshop.

(2) *The Effect of Conditions of Deposition (Acidity) on Structure.*

This can best be seen if the conditions obtaining during the formation of the deposit be set side by side with its structure. The periods into which the whole time of deposition is divided clearly correspond with the formation of the different types of structure seen in sequence in Fig. 1.

TABLE II.

Time (Hours).	Conditions.	Structure.
1st period 4	Periodical small additions.	Fibrous to lenticular.
$1\frac{1}{3}$	No further addition of acid, nor other interference with the deposition process.	Gradual change from fibrous to normal.
after 5	Considerable addition of acid.	Complete change of structure—normal to extremely fine-grained (structureless at low magnification).
$1\frac{2}{3}$	No further addition of acid.	Change in structure from extremely fine-grained to fibrous.
2nd period $2\frac{1}{4}$	Solution acid at the start. No change in the conditions except such as are caused by the electrolysis itself.	Gradual change from fibrous to coarse-grained.

The conclusions which, it is suggested, can be drawn from the observations contained in Table II. are:—

1. Acidity causes the deposit to possess a fibrous structure: excess of acid causes the structure to be of extremely fine grain.

2. As the acid diminishes in concentration the structure of the deposit change from fibrous to the normal type.

3. Undisturbed deposition results in a structure that becomes coarser and coarser in grain size as the deposition continues. It may be added that this increasing coarseness is marked, macroscopically, by increase in the size of the crystals on the surface of the deposit.

TYPES OF STRUCTURE OF ELECTRO-DEPOSITED IRON.

As the result of the examination of a very large number of specimens, the author has come to the conclusion that, as regards iron deposited from chloride baths, the great variety of structure seen in the metal, upon examination of it with a microscope, is misleading. One is apt to suppose that the types of structure characteristic of the metal is very great: it is suggested here that, really and truly, the varieties seen are variations of two characteristic types. These two characteristic types are they which have been several times referred to in the foregoing as—

(1) the *normal*, and
(2) the *fibrous*.

Of these, the former does not actually occur; it is the standard or model to which the structures of deposits formed under given sets of conditions are referred—which they more or less closely approximate.

The "Normal" Type of Structure.

A deposit of true normal structure would, in section, appear as though it consisted of grains that, all of them, possessed the shape of the longitudinal section of a cone, the boundaries of each grain forming the letter V. The size of grain and the magnitude of the angle of the V vary from grain to grain. It is as if the deposit were composed of a multitude of cones of various dimensions, all situated with their solid angles towards the base metal on which the deposit is formed. This is the type of structure to which approximation is more or less close where the deposit is formed under one set of conditions, which is characterised by absence of motion —whether of electrolyte or electrode—and neutral reaction. A deposit formed in a "still" vat and neutral solution will approximate more or less closely to the normal type of structure. The closeness to which the normal structure is approached depends, in each case, upon the particular set of conditions that has obtained during the formation of the deposit. Temperature, current density, concentration, absence or presence of floating matter (oxide or other) suspended in the solution, and other factors—all and each—influence or affect the degree of proximity to the normal. But such factors do not, any one or all of them together, cause a change to a completely different type of structure: the varieties of structure produced by the operation of such factors are varieties of the normal type. It is suggested that a general survey of the forty or so micrographs contained in the report on electrolytic iron before referred to shows that this last statement is true—at least in regard to differences produced by temperature and current density changes. The differences effected by these factors result, in fact, from concentration changes—alterations in the concentration of metal ions in the immediate neighbourhood of the cathode. And hence, concentration may be added to temperature and current density as a factor that affects the variety of the normal type of structure that a deposit will have: like these it does not change the type.

The "Fibrous" Type of Structure.

This, the alternative, type of structure seen in iron deposits formed in the chloride baths is, in longitudinal section, characterised by an appearance suggesting that the deposit is composed of a mass of threads or fibres situated at right angles to the cathode surface. The fibres may (and do) vary in thickness from sample to sample, but the form of the grains has nothing in common with that of those of the normal type of structure. This type of structure is quite characteristic of deposits formed in (i) a well-agitated solution, or (ii) a bath that contains free acid. If two baths be made up that differ only in that the one contains free acid while the other is neutral in reaction, the deposits formed in them, as "still" baths, under like conditions of deposition, will differ in that the deposit formed in the acid bath will possess the fibrous structure, while that laid down in the neutral bath will possess a structure of the normal type. This is shown by the alteration of *type* of structure, caused by acid addition, in the deposit that has been considered above. It is true that, for the formation of this deposit, one bath only was used; but addition of acid to the neutral solution in effect resulted in the constitution of an acid bath in all respects similar to the neutral bath, except for the presence of free acid. The change in type of structure, resulting from the addition of acid, was always one from normal to fibrous, marked by a change in the macroscopic appearance of the deposit from coarsely crystalline to bright, metallic, and, to the eye, non-crystalline. It will be shown elsewhere that this change may be brought about so suddenly that the form of the surface deposit existent at the moment when the acid is added can be fixed, so to say (*v.* Fig. 2); and this fact may be put to an interesting purpose.

Again, if two baths be made up that are in composition alike, and deposits formed in them under otherwise the same conditions, except that, in the one case, there is no mechanical agitation, while, in the other, either the solution is well agitated or the cathode is moved (fixed on the end of a rotating spindle, say), then the deposit formed in the "still" vat will possess the normal structure, while that formed in the other will be fibrous. The difference of type of structure brought about by the difference—absence or presence of mechanical agitation (or movement)—occurs every time. It is not a chance effect. It is not suggested that *any* degree of agitation is sufficient to effect the change. Concentration or convection currents will not, it seems, produce it; nor will liquid diffusion or the movement due to gas evolution at the cathode do so. The requisites for the formation of the fibrous structure seem to be either (*a*) constancy of concentration of metal ions in the cathode layer of electrolyte, or (*b*) presence of free acid; and the effect of mechanical agitation is, *ceteris paribus*, to maintain constant the necessary concentration of metal ions in the cathode area.

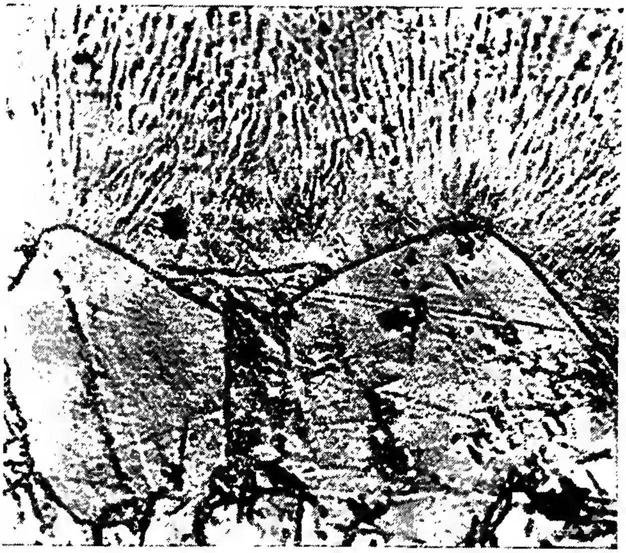
The Connection Between the Normal and the Fibrous Types of Structure.

It has been seen that a gradual change of structure occurs—from fibrous to normal—as an acid solution changes gradually to neutral. It has also been shown that a change occurs in the reverse direction when acid is added to a neutral, but that the change is more or less (sometimes, quite) sudden. Similarly, in the case of an agitated solution, when this is neutral in reaction, stoppage of the agitation results in a change of structure from fibrous to normal. A change from one type to the other may, then, occur, and the change may be gradual—at any rate in one direction, namely, fibrous to normal. Nevertheless, it is suggested that the two types of structure are separate and distinct, each type resulting from definite and known conditions which it is known beforehand will produce that type. Varieties of each type may and do occur; but so far as the author's experience goes, these varieties of type are as distinct as the types themselves. For instance, variation of a condition of deposition when the essential requisites to the formation of the fibrous structure obtain will cause a variation of the fibrous type: the variety will not be one of the normal type.

On the Effect of the Composition of the Electrolyte on the Structure.

The foregoing considerations are concerned with deposits from the chloride bath: the deposit of which the structure has been particularly described was formed in such an one. The question now arises: Are the same two types of structure, the normal and the fibrous, to be found in deposits formed in baths of other composition than chloride?

Solutions may differ from the chloride (1) in that they contain other acid radicals, or (2) because they contain some substance of the kind often referred to as an "addition agent," by which is usually meant an organic substance, such as a gum, oil, gelatin, a sugar, and many others. The question really becomes: What is the effect the acid radical or an "addition agent" upon the structure of an iron deposit? This matter is at present under investigation.



Shows how addition of acid may cause such complete change of structure as to fix a surface.

FIG. 3 × 1500.

SUMMARY.

It is suggested that it is shown in the foregoing that:—

1. The effect of acid upon the structure of an iron deposit formed in the chloride bath is to prevent the usual (normal) structure being obtained, and that the structure of a deposit laid down in an acid bath will be fibrous.

2. Structures found in iron deposits formed in chloride baths are varieties of two general and distinct types, namely, the normal and the fibrous; and that the type which is obtained depends upon the particular set of conditions that prevail during the deposition, the fibrous type being characteristic of deposits formed in (*a*) acid, and (*b*) agitated solutions.

3. Macroscopic features correspond to definite microscopic structure—a fact which enables the depositor to control the process more effectively.

DISCUSSION.

Mr. H. Sutton (*communicated*) : I would like to thank the author for his paper which is of great interest. The results of his experiments are a valuable addition to our knowledge of the subject.

I would like to ask the author whether, in the experiments described under A, B, and in Table II., the cathode was rotated or the solution agitated in any way. The author appears to have omitted to mention this point in describing the experiments, but refers later to the influence of deposition in a " still vat " without any reference to, or description of, the experiments in which " still vat " deposition was studied. In view of the marked influence of agitation of the solution, or rotation of the cathode on the nature of metallic deposits, it would be useful to have details of this kind along with the other particulars of the experiments. As the paper stands it is not quite clear upon what the author's conclusions on the influence of agitation are based.

It would be interesting to know whether the author has attempted to estimate the hydrogen content of any of his deposits from the Fischer bath, and in view of the fact that this bath has been said to yield deposits free from hydrogen, would he express an opinion on this matter.

The author appears not to have noticed, or to have considered unworthy of mention, several valuable papers on the structure of electro-deposited iron, in particular those of Mr. O. W. Storey and M. Jean Cournot.

Although the author has dealt with deposits from the chloride bath only, it would be interesting to have a comparison of his results with those of other investigators who have worked with various solutions.

M. Cournot claims to have identified a hydride of iron as a micro-constituent in certain samples of electro-deposited iron, and this micro-constituent appears to be removed by heat-treatment. It would be interesting to know whether the author has observed this micro-constituent in any of the deposits he has examined.

Mr. W. E. Hughes (*communicated reply*) : Most of the difficulties referred to by Mr. Sutton are dealt with in the paper. No quantitative work has been done by the author respecting the hydrogen content of iron deposited from chloride solutions.

NOTES ON THE ELECTROLYTIC REDUCTION OF GLUCOSE.

By Alexander Findlay and Vernon Harcourt Williams.

(*A Paper read before* The Faraday Society, *Tuesday, March* 22, 1921, Professor Alfred W. Porter, F.R.S., President, *in the Chair.*)

The possibility of reducing glucose electrolytically has attracted some attention in recent years, but the results obtained are somewhat conflicting. Thus O'Brien Gunn [D.R.P. 140318 (1900)], states that glucose dissolved in sulphuric acid of 1-3 per cent. concentration, can be reduced electrolytically using graphite electrodes and a cell with a diaphragm, the current density at the cathode being 0·15 amp. per square decimetre. A yield of mannitol amounting to 98 per cent. of the theoretical is claimed to have been obtained.

W. Löb (*Biochem. Zeitschr.*, 1909, **17**, 132; **21**, 102; *Zeitschr. Elektrochem.*, 1910, **16**, 1) on the other hand, failed to obtain this satisfactory result, and was led to conclude that both the anodic and cathodic electrolysis of glucose leads to an equilibrium between glucose, a pentose, formaldehyde, and lower carbohydrates, the cathodic reduction causing the equilibrium to shift in favour of the production of the lower compounds.

As the reduction of glucose to the corresponding hexahydric alcohol is in itself a process of importance, it seemed worth while to investigate the electrolytic process more fully, and, more especially, to study the effect on the reduction of variation of the temperature, current density, and current concentration. Although, as the result of our investigation, negative results, as regards the production of hexahydric alcohol, have been obtained, we desire to communicate some notes on our work which may prove of value in connection with this problem.

The method and apparatus employed were essentially those used by Tafel (*Zeitschr. Physikal. Chem.*, 1900, **34**, 187), in his studies on electrolytic reduction. A closed cell was employed as cathode chamber and the volume of hydrogen evolved during electrolysis was compared with that evolved from a hydrogen voltameter placed in series with the electrolytic cell. The difference in the volume of hydrogen evolved in the two cells represents the amount of hydrogen used up in the reduction.

The glucose used was "extra pure" glucose supplied by British Drug Houses, Ltd. Examined polarimetrically it gave a rotation corresponding with a purity of 99·87 per cent.

In most of the experiments lead electrodes were employed, and as Tafel has shown that the presence of metal impurities has a very unfavourable influence on the cathodic reduction, care was taken to ensure the purity of the lead electrodes employed. The purity of the lead was tested by analysis of the surface layers and the results of analysis were also confirmed by a repetition of Tafel's experiments on the reduction of caffein. This control served also to show that our method of working was satisfactory.

In the first series of experiments, carried out at the ordinary temperature, 14° to 17, the current density employed was 0·16 amp. per 100 sq. cm., and the solutions contained 1, 3, and 10 per cent. of glucose in 3 per cent. sulphuric acid. In all cases the rate of absorption of hydrogen fell off rapidly, practically to zero, and the total amount absorbed corresponded with no more than about a 2 per cent. reduction of glucose. (See Table I.) In the following table, *t* is the total time in minutes from the commencement of the experiment; T, the time in minutes from the commencement ot the experiment to the middle of each period during which successive readings of the burette were made; *e*, the volume in c.c. of gas evolved in the electrolytic cell; *v*, the volume in c.c. of gas evolved in the voltameter; E, the rate of evolution of gas in the electrolytic cell in c.c. per minute; V, the rate of evolution of gas in the voltameter; R, the rate of absorption of gas in c.c. per minute.

TABLE I.

Cathode liquid: 1 per cent., solution of glucose in 3 per cent. sulphuric acid.
Current density: 0·16 amperes per 100 sq. cm.

t.	T.	*e*.	*v*.	E.	V.	R.
0	2	0	0	0·125	0·300	0·175
4	6	0·5	1·2	0·187	0·262	0·075
8	10	1·25	2·25	0·212	0·312	0·100
12	14	2·1	3·5	0·250	0·300	0·50
16	18	3·1	4·7	0·262	0·287	0·025
20	22	4·15	5·85	0·250	0·287	0·037
24	26	5·15	7·0	0·262	0·300	0·038
28	33	6·2	8·2	0·270	0·285	0·015
38	45	8·9	11·05	0·271	0·285	0·014
52	57	12·7	15·05	0·280	0·285	0·005
62	67	15·5	17·9	0·275	0·290	0·015
72		18·25	20·8			

The total volume of hydrogen absorbed in the above experiment over the period of 72 minutes was only 1·42 c.c. at N.T.P.

Similar results were obtained on commencing the electrolysis with a peroxidised lead cathode, and also when the sulphuric acid was replaced by sodium bisulphate as electrolyte.

Influence of Temperature.—On carrying out the electrolysis at a temperature of about 44°, no better results were obtained. The influence of temperature was found to be practically inappreciable; if anything, the hydrogen absorption was diminished.

Graphite Electrodes.—On using electrodes of gas carbon or of Acheson graphite the results were similar to those obtained with a lead electrode.

Current Density and Current Concentration.—In general, reduction of the cathodic current density is accompanied by a slight increase in the efficiency of electrolytic reduction, but although we carried out an experiment with a current density somewhat lower than that previously employed (0·102 instead of 0·16 amp./sq. dcm.), no appreciable improvement was observed. It has, however, been shown by Tafel (*loc. cit.*), that current concentration (current per unit volume of solution), has a greater influence than current density. Experiments were therefore carried out in which the current concentration was varied between the limits of 0·04 and 0·444 amps. per 100 c.c. The results obtained showed that with increase of current concentration, the absorption of hydrogen also increases but, as in previous experiments, falls off rapidly with time.

During the progress of these experiments it was observed that the cathode solution, after electrolysis, possessed a sharp aldehydic odour, and the cathode was found to be coated with a film of slimy appearance. This film was soluble in alcohol. As it was thought that the production of this film might be the cause of the rapid falling off of the volume of hydrogen absorbed by the depolariser, experiments were carried out in which the same solution was subjected to repeated electrolysis, the cathode, after each run, being treated with boiling alcohol to remove the film produced. After each treatment of the cathode it was found that a further absorption of hydrogen took place, but that this absorption again rapidly fell off to zero. Using a current concentration of 0·444 amps. per 100 c.c., and a cathode solution of 20 per cent. glucose in 5 per cent. sulphuric acid, the following successive absorptions of hydrogen were realised: 28·5, 8·1, 32·2, 52·8, 30·2, 24·1, and 23·5 c.c. The total absorption amounted therefore to 199·4 c.c., or 40·1 per cent. of the theoretical amount. During these experiments, which extended over several hours, a considerable loss of glucose took place by diffusion from the cathode cell. In the most favourable case, where the highest current was employed, the loss amounted to nearly 30 per cent.; where lower currents were employed and the duration of the electrolysis was therefore greater, the loss by diffusion was of course also greater. Attempts to diminsh diffusion by use of a membrane of copper ferrocyanide deposited in the wall of the porous cathode cell, were not successful.

Since the foregoing experiments seemed to indicate that a considerable proportion of the glucose had been reduced, an attempt was made to isolate the supposed product of reduction, the hexahydric alcohol. The solution was neutralised with chalk to remove sulphuric acid, and was then evaporated on the water bath. The syrupy liquid was dissolved in concentrated hydrochloric acid and the acid solution shaken with benzaldehyde and allowed to stand for several days. By this means, mannitol or sorbitol, if present, can be precipitated as a condensation product with benzaldehyde (Meunier, *Compt. rend.*, 1888, **107**, 910). No such compound, however, was obtained, and we are therefore driven to conclude that no appreciable amount of hexahydric alcohol was produced in our electrolytic experiments.

On examining the alcoholic washings from the cathode, a lead salt was isolated which, on analysis, was found to be lead formate. Formic acid was also found in the cathode solution after electrolysis. The production of this acid in the electrolytic reduction of glucose is mentioned by Löb (*Zeitschr. Elektrochem.*, 1910, **16**, 1), who states that glucose decomposes into formic acid and a pentose. The presence of pentose in the solution we detected by the furfuraldehyde test.

Further evidence of the production of formic acid was obtained from an analysis of the gas evolved at the cathode during electrolysis. This gas was found to be not pure hydrogen but to contain about 4 per cent. of carbon monoxide, produced, presumably, by a decomposition of formic acid. The percentage of carbon monoxide varied somewhat during electrolysis, being greater during the earlier than during the later stages of the electrolysis. Although the destructive reduction of glucose with production of formic acid and a pentose does not appear to take place to a very large extent, the formation of these compounds may play an important part in the process of electrolytic reduction if, as seems probable, it is the formic acid which leads to the formation of the film on the cathode with consequent diminution or prevention of further reduction.

As a result of our experiments, which are in harmony with the results obtained by Löb, we are forced to conclude that, contrary to the claims of O'Brien Gunn, no hexahydric alcohol is produced in the electrolytic reduction of glucose.

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THE SOLUBILITY OF SMALL PARTICLES AND THE STABILITY OF COLLOIDS.

By L. F. Knapp, B.Sc., A.I.C.

(*A paper read before* The Faraday Society, *Monday, May* 9, 1921, Professor Alfred W Porter, F.R.S., President, *in the Chair.*)

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The stability of many colloids appears to be connected with the electric charge carried by the disperse phase. In this paper an attempt is made to explain this relation by consideration of the influence of the electric charge on the solubility of the particles.

Wilhelm Ostwald[1] derives thermodynamically a relation between the solubility and size of solid particles, but his expression contains a mistake in the numerical factor. Freundlich[2] discusses this error and gives the correct expression

$$\frac{RT\rho}{M}\log_e\frac{S_1}{S_2} = 2\sigma\left(\frac{1}{r_1} - \frac{1}{r_2}\right) \quad . \quad . \quad . \quad . \quad (1)$$

where R is the gas constant, T the absolute temperature, M the molecular weight of the solid in solution, ρ the density of the solid, σ the interfacial tension between the solid and its solution, and S_1 and S_2 are the solubilities of the particles of radii r_1 and r_2 respectively. These symbols will be used with the same meaning throughout this paper. If one of the particles is very large the equation may be written

$$\frac{RT\rho}{M}\log_e\frac{S_r}{S} = \frac{2\sigma}{r} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where S is the normal solubility, *i.e.*, the solubility when the particles are large and have approximately flat surfaces. In the derivation of these equations it is assumed that the particles are spherical, that the dissolved solid obeys the gas laws and that σ and ρ are independent of the size of the particles.

Lewis[3] considers the opposing effect of the surface tension and the electric charge at the surface of colloid and emulsion particles. He assumes that the particles are isolated charged spheres and that their charge is independent of their size. The surface tension exerts an inward pressure equal to $\frac{2\sigma}{r}$ while the electric charge produces an expanding pressure, which is given by the expression $\frac{q^2}{8\pi K r^4}$, where q is the charge and K the dielectric constant of the medium in which the particles are dispersed. When these opposing pressures are equal, *i.e.* when

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[1] *Zeit. Phys. Chem.*, 34, 495 (1900).

[2] *Kapillarchemie*, Leipzig, 1920, p. 143.

[3] *Koll. Zeit.*, 5, 91 (1909).

$$r = \sqrt[3]{\frac{q^2}{16\pi K\sigma}} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

the effect of curvature on the solubility is removed and the particles can exist in equilibrium with a flat surface.

This result will be demonstrated in another way from a modification of Ostwald's formula in which the electrical energy at the surface of the particle is taken into account. If the particles are considered as isolated charged spheres, the total free energy, E, at the surface of any particle is equal to the sum of the ordinary surface energy and the electrical energy,

i.e.
$$E = 4\pi r^2\sigma + \frac{q^2}{2Kr} \quad . \quad . \quad . \quad . \quad (4)$$

If M is the mass of a particle and if its density, ρ, is assumed to be the same as that of the material in bulk,

$$m = \frac{4}{3}\pi r^3\rho \text{ and } dm = 4\pi r^2\rho \, . \, dr.$$

By differentiation of equation (4) with respect to m

$$dE = \frac{1}{\rho}\left(\frac{2\sigma}{r} - \frac{q^2}{8\pi K r^4}\right)dm. \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Consider a system of two spherical particles of radii r_1 and r_2, each in equilibrium with its saturated solution, the osmotic pressures of the dissolved solids being p_1 and p_2 respectively, and let an isothermal and reversible cycle be carried out, in which a small mass dm is removed from the first particle and added to the second, then dissolved from the second particle against the osmotic pressure p_2, compressed to p_1 and deposited on the first under the pressure p_1. If the dissolved solid obeys the gas laws, as is the case when the solubility is small, it can be shown by considering the free energy changes that

$$\frac{RT\rho}{M}\log_\epsilon\frac{S_1}{S_2} = 2\sigma\left(\frac{1}{r_1} - \frac{1}{r_2}\right) - \frac{q^2}{8\pi K}\left(\frac{1}{r_1^4} - \frac{1}{r_2^4}\right) \quad . \quad . \quad (6)$$

If one of the particles is very large the equation approximates to

$$\frac{RT\rho}{M}\log_\epsilon\frac{S_r}{S} = \frac{2\sigma}{r} - \frac{q^2}{8\pi K}\cdot\frac{1}{r^4} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where S_r is the solubility of particles of radius r, and S is the normal solubility.

Equation (7) may be written in the exponential form

$$S_r = S\epsilon^{\frac{\alpha}{r} - \frac{\beta}{r^4}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where α and β are constants and equal to $\frac{2\sigma M}{RT\rho}$ and $\frac{q^2 M}{8\pi KRT\rho}$ respectively.

Differentiation of (8) gives

$$\frac{dS_r}{dr} = S\epsilon^{\frac{\alpha}{r} - \frac{\beta}{r^4}}\left(\frac{4\beta}{r^5} - \frac{\alpha}{r^2}\right) \quad . \quad . \quad . \quad (9)$$

which is equal to zero when

$$r = \sqrt{\frac{4\beta}{\alpha}} = \sqrt[3]{\frac{q^2}{4\pi K\sigma}} \quad . \quad . \quad . \quad (10)$$

When r has this value the second differential of (8) has a negative value, and, therefore, the solubility is a maximum at this point. Also when r approaches zero, S_r approaches zero; when r is infinite, S_r is equal to S. These results are shown graphically in Fig. 1.

For a particle with a finite radius to be in equilibrium with a flat surface the solubility must be equal to S. From equation (8) this value for S_r is obtained when

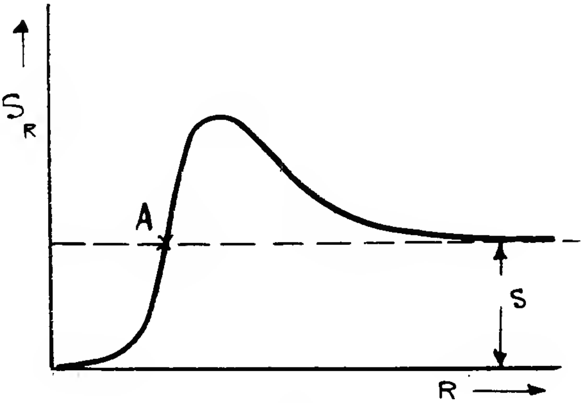

FIG. 1.

$$\epsilon^{\frac{\alpha}{r} - \frac{\beta}{r_4}} = 1$$

i.e. when

$$\frac{\alpha}{r} - \frac{\beta}{r^4} = 0$$

or

$$r = \sqrt[3]{\frac{\beta}{\alpha}} = \sqrt[3]{\frac{q^2}{16\pi K\sigma}}$$

which is the same expression as that given by Lewis. This equilibrium value of the radius is shown in Fig. 1. as the ordinate of the point A.

According to Helmholtz's theory there arises at the interface of disperse particles and the dispersion medium an electrical "double-layer"; that is, a charged particle is surrounded by oppositely charged ions or molecules which lie at a distance from its surface. This distance has been estimated by various methods at about 5×10^{-7} cm.[1] If, then, each particle is regarded as a rigid double-layer condenser, its electrical energy is given by the expression $\frac{q^2 d}{2Kr(r + d)}$, where q is the quantity of electricity on each layer,

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[1] G. V. Hevesey, *Koll. Zeit.*, **21**, 129 (1917).

d the distance between the layers, and r the radius. For most colloid and emulsion particles d is negligible compared with r and the simpler formula $\frac{q^2 d}{2Kr^2}$ holds. If this expression is employed instead of that used above, the relation between solubility and size of particle becomes

$$\frac{RT\rho}{M} \log_\epsilon \frac{S_r}{S} = \frac{2\sigma}{r} - \frac{q^2 d}{2\pi K r^5} \quad . \quad . \quad . \quad . \quad (11)$$

or

$$S_r = S\epsilon^{\frac{\alpha}{r} - \frac{\beta}{r^5}} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where α and β are constants equal to $\frac{2\sigma M}{RT\rho}$ and $\frac{Mq^2 d}{4\pi K \,.\, RT\rho}$ respectively. The curve of this equation has the same general shape as that of equation (8) (Fig. 1); the solubility is a maximum when

$$r = + \sqrt[4]{\frac{5q^2 d}{8\pi K\sigma}} \quad . \quad . \quad . \quad . \quad (13)$$

and is equal to that of large particles when

$$r = + \sqrt[4]{\frac{q^2 d}{8\pi K \,.\, \sigma}} \quad . \quad . \quad . \quad . \quad (14)$$

In many colloidal solutions and emulsions the particles are all approximately the same size and there appears to be a "critical" radius which they strive to obtain. A good example of this critical radius has been given by Lewis.[1] He prepared oil-water emulsions by several methods and in each case found that the radius of the oil drops was $4{\cdot}3 \times 10^{-4}$ cm. The charge also was the same and amounted to $4{\cdot}4 \times 10^{-7}$ E.S.U. These facts can be explained by the results of Lewis' theory or by the similar results obtained when the double-layer theory is introduced, only when the dispersed substance is present both as small particles or drops and in comparatively large masses having approximately flat surfaces. In this case the small particles would increase or decrease in size until their solubility became the same as that of their substance in mass. This condition is realised when an oil-water emulsion is made and only part of the oil is emulsified, but it is not so for most colloidal solutions, especially those prepared by chemical methods. In such cases the disperse phase is at first formed in small particles. According to equation (8) or (12), provided they were of sizes less than that at which solubility is a maximum, they would become uniform in size, since the solubility increases with the radius, but the uniform size at which they would arrive would be determined by the number and size of the particles first formed, and would lie between the extreme sizes of the latter. It would not generally be at that size at which the solubility is the same as the substance in mass.

In some preliminary experiments made by the author on a silver bromide "emulsion" prepared by mixing a solution of ammonium bromide containing gelatine with an ammoniacal solution of silver nitrate, it was observed that the particles of silver halide, if examined soon after their formation, were very small and of uneven size, the largest being about $0{\cdot}5 \times 10^{-4}$ cm. in diameter (Fig. 2), but when the mixture was heated at 45° C. for 40 minutes, they were all about $0{\cdot}5 \times 10^{-4}$ to 1×10^{-4} cm. in diameter (Fig. 3). Here the grains became uniform, but they were somewhat bigger than the largest of the original particles from which they were formed. If either of the equations (8) and (12) correctly represents the relation between solubility and size of particle, it must be assumed, in order to explain these facts, either that the charging of the particles does not take place instantaneously at their formation but occurs during their initial growth, or that the completion of precipitation is delayed in some manner by the presence of gelatine, with the result that the solution is at first supersaturated with respect to all particles present and only slowly deposits its excess of dissolved silver bromide. The first assumption is quite possible inasmuch as the charge on the particles is probably due to adsorption of ions, and some adsorption processes are known to take place slowly.

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[1] *Zeit. Chem. Ind. Koll.*, 4, 211 (1909).

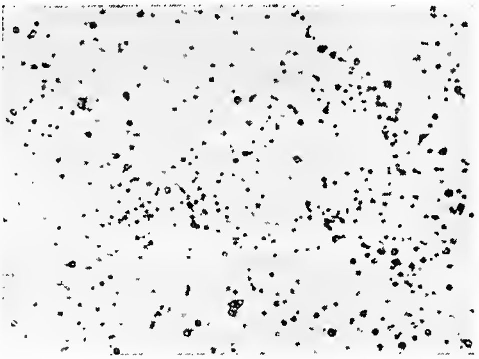

Fig. 2.

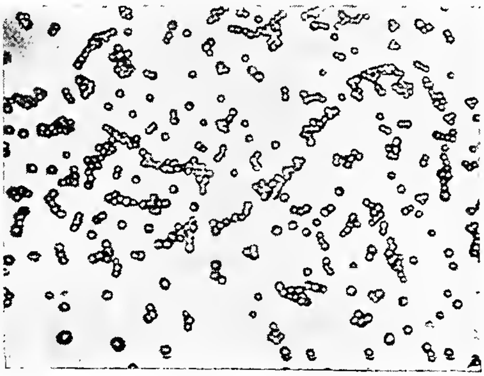

Fig. 3.

In this direction it would be of great interest if experiments could be performed in which the concentration and the sizes of the particles of the disperse phase, the concentration of the disperse substance in true solution and the mobility of the particles in an electric field could be determined simultaneously and continuously during the growth of the latter to their stable size. The silver halide gelatine emulsion, mentioned here, is unsuitable for this purpose owing to the difficulty of filtration and the great conductivity of the ammonium nitrate formed during the precipitation of the silver halide.

If, however, the particles are charged as soon as they are formed and the precipitation is completed almost instantaneously, the theory developed here, although predicting the uniformity of the particles finally obtained, fails to account for the fact that they are larger than all those present immediately after the formation of the emulsion. To explain this it would appear that the solubility radius curve must pass through a minimum value. If this is so, the particles at first grow irregularly; the larger ones being less soluble grow at the expense of the smaller which soon completely dissolve. When the radii of some of the particles exceed that at which the solubility is a minimum, the unevenness begins to disappear, and finally all the particles approach the same size. They will be bigger than all those originally present, and not smaller than those of which the solubility is a minimum.

An expression, having a minimum value for the solubility, is obtained if the charge on each side of the double layer is considered as being proportional to the third power of the radius. Let $q = ar^3$ where a is a constant. The electrical energy of any particle is

$$\frac{q^2 d}{4Kr^2} = \frac{a^2 . d . r^4}{2K} \quad . \quad . \quad . \quad (15)$$

when d is small compared with r, and the total free energy at the surface of the particle is given by the expression

$$E = 4\pi r^2 \sigma + \frac{a^2 d}{2K} . r^4 \quad . \quad . \quad . \quad . \quad (16)$$

On differentiation with respect to m

$$dE = \frac{1}{\rho}\left(\frac{2\sigma}{r} + \frac{a^2 d}{2\pi K} . r\right) dm.$$

The second term $\frac{a^2 d}{2\pi K} . r . \frac{dM}{\rho}$ which represents the increase of electrical energy E_e may be regarded as the algebraic sum of the two expressions

$$\left(\frac{\partial E_e}{\partial v}\right)_{q \text{ const.}} dv \quad \text{and} \quad \left(\frac{\partial E_e}{\partial q}\right)_{v \text{ const.}} dq$$

where dv and dq are the increases in volume and charge corresponding to the increase of mass dm. The first expression is the work done by the electrical pressure acting through the volume dv, the charge being constant, and the second is the work done on the particle when its charge is increased at constant volume by the amount dq.

By consideration of the same thermodynamic cycle as before the relation between solubilities S_1 and S_2, of particles of radii r_1 and r_2 is

$$\frac{RT\rho}{M} \log_e \frac{S_1}{S_2} = 2\sigma\left(\frac{1}{r_1} - \frac{1}{r_2}\right) + \frac{a^2 d}{2\pi K}(r_1 - r_2) \quad . \quad . \quad (17)$$

In this case the equation cannot be simplified by taking one of the radii as very large. If, however, r_2 is regarded as a constant having the finite value c the corresponding solubility S_c is constant, and the variation of solubility with size of particles is expressed by the equation

$$\frac{RT\rho}{M}\log_e\frac{S_r}{S_c} = \frac{2\sigma}{r} + \frac{a^2d}{2\pi K} + k \quad . \quad . \quad . \quad (18)$$

where k is a constant and equal to $\left(\frac{2\sigma}{c} + \frac{a^2d}{2\pi K}\cdot c\right)$.

Equation (18) may be written in the exponential form

$$S_r = S_c e^{\left(\frac{\alpha}{r}+\beta r+\gamma\right)} \quad . \quad . \quad . \quad . \quad . \quad (19)$$

where α, β and γ are constants and equal to $\frac{2\sigma M}{RT\rho}$, $\frac{a^2 . d . M}{2\pi KRT\rho}$ and $\frac{kM}{RT\rho}$ respectively.

When r has a small positive value approaching 0 and when $r = \infty$, $S_r = \infty$.

By differentiation $\qquad \frac{dS_r}{dr} = S_c e^{\frac{\alpha}{r}+\beta r+\gamma}\left(\beta - \frac{\alpha}{r^2}\right)$

which is equal to zero when

$$r = \pm\sqrt{\frac{\alpha}{\beta}} = \pm\sqrt{\frac{4\pi K\sigma}{a^2d}} \quad . \quad . \quad . \quad (20)$$

When r has the positive value the second differential of equation (19) is positive, and therefore there is a minimum solubility at this point. These results are shown graphically in Fig. 4.

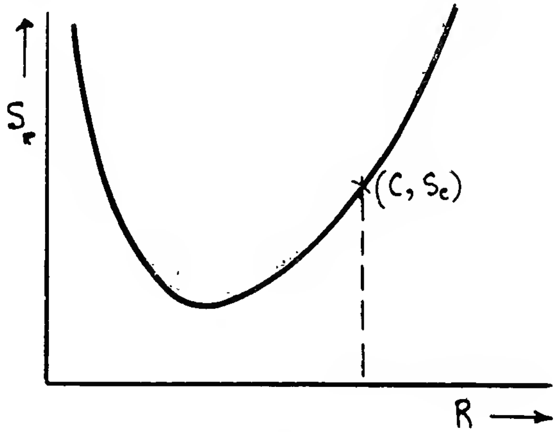

FIG. 4.

Although this equation explains the stability of colloids, the assumption, on which it is based, that the charge is proportional to the third power of the radius, does not appear to be in accordance with Lamb's theory of the motion of charged particles in an electric field.[1] This theory is expressed in the equation

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[1] *Brit. Assoc. Report*, 495 (1887).

$$V\left(\frac{l}{d}\right) = \frac{4\pi\eta v}{KX} \quad . \quad . \quad . \quad . \quad . \quad (21)$$

where V, l and d are respectively the potential difference, the "facility" of slip and the distance between the two layers of electricity, η and K are the viscosity and the dielectric constant of the medium or continuous phase, X is the potential gradient of the electric field, and v the velocity of the particles. Lamb gives reasons for taking $\frac{l}{d}$ as equal to unity. His equation then becomes

$$V = \frac{4\pi\eta v}{KX} \quad . \quad . \quad . \quad . \quad . \quad (22)$$

It is known that for the same medium the mobilities of many colloids, irrespective of the size of their particles, have approximately the same value. From equation (22) it follows that the potential difference V must have the same value in each case. If then, V is constant, and if, as has been assumed throughout, the capacity of a particle is that of a rigid double layer, spherical condenser, the charge is given by the expression

$$q = \frac{VK}{d}r^2$$

when d is small compared with r. Hence the charge is proportional to the second power of the radius and not to the third.

On the other hand the modification of Ostwald's relation, obtained when the charge varies as r^2, does not account for the stability of colloids. For, when $q = br^2$ where b is a constant equal to $\frac{VK}{d}$, the relation between solubility and size of particle becomes

$$\frac{RT\rho}{M}\log_e\frac{S_r}{S} = \left(2\sigma + \frac{b^2d}{4K}\right)\cdot\frac{1}{r} \quad . \quad . \quad . \quad . \quad (23)$$

or

$$S_r = Se^{\frac{\alpha}{r}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

where α is a constant equal to $\left(2\sigma + \frac{b^2d}{K}\right)\frac{M}{RT\rho}$.

The curve of this equation has the same form as that of Ostwald's. The solubility decreases continuously with increase of radius until it becomes asymptotic to S, the normal solubility of large particles.

In the derivation of these equations it has been assumed that the surface energy σ, is independent of the radius. Most colloid particles are large compared with the molecules and in such cases, no alteration of the surface energy, analogous to that which takes place in thin films is to be expected. It must be remembered, however, that the adsorbed ions, which constitute the electrical layers, may produce not only the electrostatic effect considered here, but also an alteration in the surface energy in the same way as adsorbed substances in general. The value of σ therefore, may depend on the radius of the particles; and the manner of its variation will be connected, as will that of the electrical charge, with the way in which the concentration of the adsorbed ions alters.

Except in the first case (equation 4), the calculations of the electrical energy have been based on the assumption that the particles are rigid, double layer condensers. That this assumption is not strictly correct is shown by the fact that colloid particles move under the influence of an electric field. For this reason the expression for the electrical energy may need some modification.

In the analysis of the various equations only positive values of r which

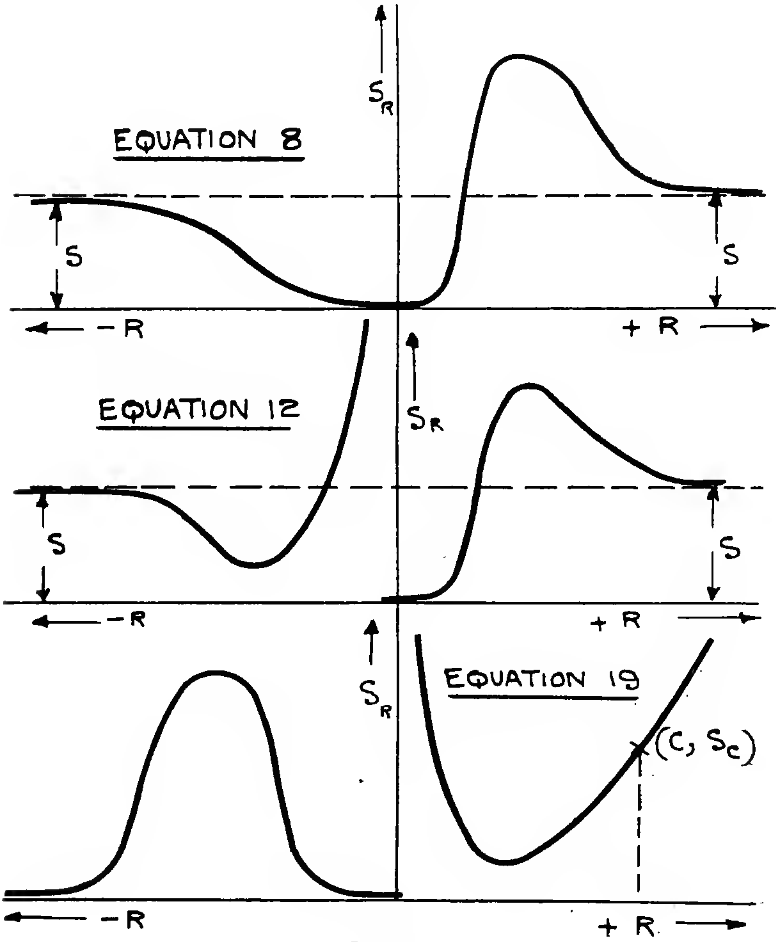

FIG. 5.

represent convex surfaces, have been considered. The negative values, which correspond to concave surfaces, may find some application in the case of emulsions, when the solubility of the continuous phase in the drops of the disperse phase is investigated. In Fig. 5 the general form of the curves of the equations (8), (12), and (19) are given for positive and negative values of the radius.

THE PROBLEM OF THE FUEL CELL.

By E. K. Rideal and U. R. Evans.

(*A paper read before* The Faraday Society, *Monday, May* 9, 1921, Professor Alfred W. Porter, F.R.S., President, *in the Chair.*)

[*First received December* 20, 1920.]

During the first half of the year 1914 we were engaged on some experiments upon "fuel cells," mainly on the indirect type. The work was interrupted by the outbreak of the war whilst still in the preliminary stages, and there is little chance that we shall be able to resume our researches. At the time of the interruption, however, we had—as a result both of our study of the literature of the subject, and also of our experimental work—become convinced that there is still a great deal of misconception regarding the essential character of the problem to be solved, and particularly regarding the points which should be recorded in a research in order to arrive at a measure of the success obtained. Some recent publications on the subject of fuel cells lead us to think that the misconception is shared, in some instances, by those who are doing practical work on the subject.

We should consider ourselves justified, therefore, in stating our views on this subject, even if our practical work had been entirely fruitless. In addition we think that a short description of our experimental results will be of use to future workers. Many of the attempts led to negative results; but since we are in every case able to assign a definite cause for failure, a summary of these attempts may be of some value in enabling future investigators to avoid failure. Some of the lines of investigation, on the other hand, were developing in a hopeful manner. When the work came to an end it was, however, impossible to draw definite conclusions, as there were clearly many difficulties to be solved. Every experiment described in this paper was—at the time when it was performed—regarded as merely a preliminary experiment made with a view to ascertaining whether some particular form of cell was worthy of extended study.

Part I.—General Principles.

The Fundamental Purpose of a Fuel Cell.—The economic importance which would attach to the invention of an efficient fuel cell is very generally understood. In this country, and most others in which waterpower is not plentiful, most of the electrical energy required for industrial and domestic consumption is derived, ultimately, from coal or other fuel. The energy efficiency of the conversion of coal energy to electrical energy is always small. According to numbers given in Allmand's "Applied Electrochemistry," if the boiler, steam-engine, and dynamo is used for the conversion, 10-15 per cent. of the potential energy of coal may be converted to electrical energy; if, alternatively, we make use of the gas-producer, gas-engine and dynamo, the efficiency may be rather higher, perhaps 25 per cent. Now part of the big loss of energy is due to factors capable, at least theoretically, of being made very small as the design of the plant involved is improved: for instance, the part of the loss due to the fact that the heat-conducting materials employed are not perfect conductors, and the heat-insulating materials are not perfect insulators. These and other "human" failings on the part of the plant will no doubt be lessened in the future by the ingenuity of designers. But there is one cause of serious loss which apparently is insuperable; the maximum efficiency of any heat engine working between temperatures θ_1 and θ_2 can never exceed

$$\frac{\theta_1 - \theta_2}{\theta_1}$$

the efficiency of the "reversible" engine dreamed of—but, unfortunately, not marketed—by Carnot. The loss due to this cause can, of course, be reduced by making θ_1 high and θ_2 low, but it is unlikely that the wastage will ever become negligibly small. Therefore the employment of any form of heat engine as an agent in the transformation of coal energy to electrical energy is—for fundamental thermodynamical reasons—wasteful.

On the other hand, if natural fuel could be used—directly or indirectly—as the consumable material in a primary battery, there is no fundamental reason why a high energy efficiency should not be attained. If, for instance, natural fuel consisted of metallic zinc—not coal—it could be burnt in primary cells to give electrical power directly at an efficiency which would probably exceed 90 per cent. But, in the case of an electric cell in which coal is the attackable electrode, it is very difficult to obtain high energy efficiency at all, and, although an energy efficiency of about 50 per cent. has been obtained in one semi-direct fuel cell, the capital cost of such a cell is so high compared to the amount of power produced, that the erection of a cell on any design hitherto suggested must necessarily be unremunerative, and is not for one moment to be thought of as a "commercial proposition".

Before dealing with the essential difficulties attaching to the "fuel-cell problem," some sort of classification of fuel cells should be attempted. We propose to classify them in this way:—

1. *Direct Fuel Cells*, in which the coal, or some form of solid carbonaceous fuel prepared from it, is used as the attackable electrode of the combination.
2. *Semi-Direct Fuel Cells*, in which some gaseous fuel such as

   (*a*) carbon monoxide, or
   (*b*) hydrogen

derived from coal is used to saturate the negative electrode, and thus act as the attackable electrode-substance.

3. *Indirect Fuel Cells*, which may be subdivided into

(*a*) *Oxidation-Reduction Cells*, in which the reducing and oxidising agents present in solution in the two compartments are regenerated by treatment with fuel and air respectively; the regeneration may be conducted either within the cell, or in an external vessel.

(*b*) *Metal-Electrode Type* in which a metal, obtained by reduction with fuel, is employed as the attackable electrode. Strictly, the ordinary primary cell (Leclanché or dichromate) is a fuel cell of this class, but the energy efficiency of zinc metallurgy is very low; and it would be particularly difficult, after recovering the zinc as sulphate or chloride from the exhausted cell, to reduce this same zinc to metallic form without serious loss.

Under these headings it is possible to classify the various forms of fuel cells hitherto investigated:—

TYPE (1) By combining a carbon electrode with an air (oxygen) electrode, so as to produce the combination

Carbon | Electrolyte | Oxygen,

an E.M.F. should be obtained, the value of which, calculated from the free energy of the reaction

$$C + O_2 = CO_2,$$

should be 1·05 volts.

The E.M.F. quoted is the E.M.F. which the cell should "balance". The value of 1·05 volts will only be reached when the cell is producing no current, and hence no energy. As soon as a cell begins to furnish current the E.M.F. will always drop below its equilibrium value, the drop being greater the higher the current density furnished by the cell. This phenomenon, which is known as *polarisation*, is shown by all cells. The E.M.F. of even the Daniell cell drops well below 1·096 volts when it provides a current, and this loss (although partly due to the fact that a fraction of the P.D. falls within the cell itself) is also caused by an alteration in value of the P.D.'s at the two electrodes. Polarisation has been attributed by Leblanc to the limited velocity of the electrodic reactions, and by Nernst to the limited rate of diffusion in the layer next to the electrode. Undoubtedly it is, in general, due to both causes.

The polarisation—or drop in the E.M.F. with the increase of current—is far greater in the case of a cell in which carbon (or indeed any non-metal) is the attackable electrode than in the case where zinc is employed. This is made clear by curves given in Fig. 1 based upon results obtained by Taitelbaum.[1] The comparatively serious drop in the E.M.F. (which is mainly due to the carbon electrode) has been ascribed to the fact that the electrolytic corrosion of the zinc is due to a simple change such as

$$Zn = Z\ddot{n} + 2e,$$

whilst, at the carbon electrode, no such simple change occurs, because carbon does not form a cation. If, however, the kind of views advanced by Sackur[2] and others regarding the anodic corrosion of metals is accepted, an anode must be regarded rather as a destroyer of anions than as a provider of cations, and the explanation given above falls to the ground.

Perhaps, therefore, it is best to state it as an experimentally proved fact that carbon—and other non-metals—enter into electrodic reactions at a small velocity only, and not to attempt any explanation.[3] The velocity increases, and therefore the polarisation becomes less, as the temperature rises. Hence there is an advantage—which often amounts to a necessity—in working at elevated temperatures. In so far as polarisation is caused by slow diffusion efficient stirring of the bath will lessen the trouble; this latter factor, however, becomes more marked in cells of type 3.

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[1] *Zeitsch. Elektrochem.*, 16 (1910), 286. [2] *Ibid.*, 14 (1908), 607.

[3] In this connection the recent work on the irreversible adsorption of oxygen by gas-charcoal is of great significance.

The earliest attempt at a direct fuel cell was made as long ago as 1855 by Becquerel,[1] who melted nitre in a platinum vessel, plunged a carbon rod into the fused salt, and, using the carbon and platinum as the two electrodes, obtained a current. Jablochkoff in 1877 used a similar cell, but employed cast-iron instead of platinum. Both these cells must have been of low current efficiency, the nitre attacking the carbon mainly in a manner which produced no current. As Ostwald afterwards pointed out they offend against a fundamental principle of a cell, namely, that the oxidising substance (in this case, nitre) should not be placed at the attackable electrode (here, carbon) but at the unattacked positive electrode.

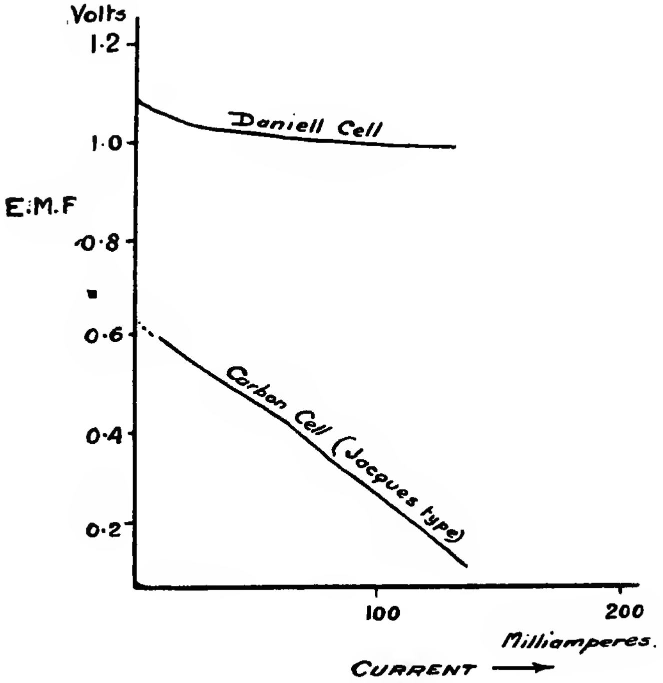

FIG. 1.

Much later, Jacques[2] designed a cell wherein fused caustic soda was contained in an iron pot, which constituted the positive pole of the battery, the iron being passive; a carbon rod plunged into the mass constituted the negative pole. Air was bubbled through the fused bath during the production of current. It has been shown, however, by Haber and Brunner,[3] that a cell of this kind is not properly a carbon/oxygen cell. The electro-motive element at the carbon pole is really hydrogen, produced indirectly by reaction between the carbon and sodium hydroxide. Moreover it was also shown that the presence of a trace of manganese as an impurity, which becomes oxidised to manganate by the air bubbled through the bath, is essential for the satisfactory working of the cell. Thus the Jacques cell should really be regarded as a

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[1] See B. Blount's "Practical Electrochemistry," 1906 edition, p. 364.

[2] *Zeitsch. Elektrochem.*, 4 (1897), 129.

[3] *Ibid.*, 10 (1904), 697, 12 (1906), 78.

Hydrogen | Manganate

cell, and belongs properly to type (2).

It was also shown that the sodium hydroxide was transformed to carbonate (or perhaps formate) during the production of the hydrogen, and therefore a considerable expenditure of energy would be demanded, periodically, in regenerating the hydroxide. For this reason alone the Jacques cell affords no solution of the problem.

An improved form of the cell was studied by Taitelbaum,[1] who through an ingenious device, divided the cell into two halves by what was virtually a porous diaphragm, and thus ensured that the manganate did not attack the carbon electrode directly. Taitelbaum added manganese dioxide in measured amounts to the positive compartment, but does not appear to have studied the rate at which the dioxide could be regenerated by aeration, although he states that "oxygen is absorbed energetically by the fused bath". He was able to show that various forms of carbon, such as coal, lignite, sawdust, sugar, or wood charcoal could be used as attackable elements. He also studied the polarisation of the cell; one cell, using prepared carbon, gave a P.D. of about 0·6 volts, when it was yielding little or no current, but the E.M.F. dropped to 0·1 volts when it was made to furnish a current of 140 milliamps.

It should be noticed that a further objection to cells of this character is the use of iron as unattackable electrode. It is difficult to ensure that it remains passive.

A more recent cell of the same character due to Read[2] has avoided two of the obvious objections to the Jacques cell. He has used thin gold foil as a cathode instead of iron, and he has used fused borax containing manganese (added as manganese dioxide) instead of fused caustic soda, as the electrolyte. He constructed a battery of six cells in series, built one on the top of the other, in a rather ingenious manner. The whole cell is contained in a shallow Battersea crucible, which arrangement provides in the cathode compartment a large surface area of contact between the fused bath and the atmosphere, with a view to maintaining the manganese in the oxidised condition. Air was not bubbled through the liquid. The attackable material at the anode is powdered coal, in which a graphite electrode cut into the form of a grid is embedded, and serves to put the whole into electrical contact with the external circuit.

He found that each cell of his battery gave an E.M.F. of 0·9 volts, and obtained a current of 185 milliamps. over a 4⅓ ohms. resistance falling at the end of an hour to 157 milliamps. This current is not unsatisfactory considering the size of cell used, but the drop is very significant. One cannot help asking, whether the regeneration of the oxidising agents (manganates and manganites) was taking place as fast as they were being used up. In cells of this type a trial run for a period greatly exceeding one hour would be advisable.

We shall return to the question of the rate of regeneration of oxidising agents in connection with cells of type (3).

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[1] *Zeitsch. Elektrochem.*, **16** (1910), 286.

[2] *Trans. Amer. Electrochem. Soc.*, **33** (1918), 89.

A rather attractive form of cell is due to Baur and Ehrenberg,[1] who used fused borax as an electrolyte, a carbon rod as anode, and fused silver saturated with air as cathode. The silver acts as an oxygen electrode. The investigators showed that if hydrogen instead of air be employed, the E.M.F. of the cell drops practically to zero, but recovers as soon as air is let in once more. The cell yields 0·95 volts, but drops to about 0·5 volts when yielding a current of 90 milliamps.

The following table summarises the cells of type (1):—

Name.	Cell.		
Becquerel . . .	Carbon . .	Fused KNO_3	Pt
Jablochkoff . .	Carbon .	Fused KNO_3	Iron
Jacques	Battery carbon ·	Fused NaOH containing trace of Mn (Aerated)	Iron
Taitelbaum . .	Coal, charcoal, etc. . .	Fused NaOH :: Fused NaOH with MnO_2	Iron
Read . .	Coal . .	Fused borax with Mn (reduced) :: Fused borax with Mn (oxidised)	Gold
Baur and Ehrenberg .	Carbon . .	Fused borax	Molten silver containing oxygen

Note.—The sign :: represents a porous partition or other device for reducing undue diffusion.

TYPE (2) If, instead of using coal as an attackable electrode, we convert it to a gaseous fuel, such as carbon monoxide or hydrogen, it should be possible to obtain electrical energy by means of a cell with gas-saturated electrodes. The theoretical E.M.F.s (approximate) obtained in the two cases are:—

$CO - O_2$ cell	1·34 volts.
$H_2 - O_2$ cell	1·23 volts.

In the burning of coal to carbon monoxide, about one-third of the energy is liberated as heat, and is probably lost. For that reason carbon monoxide cells are inherently wasteful. The fact that the carbon monoxide cell gives a higher theoretical E.M.F. (1·34 volts) than the coal cell (1·05 volts) need occasion no surprise, if it is remembered that (for the same consumption of carbon) only half the current is produced in the carbon monoxide cell. As a matter of fact, the theoretical E.M.F. of the carbon monoxide cell drops very much as the temperature rises, as is shown by the following numbers given by Allmand:—[2]

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[1] *Zeitsch. Elektrochem.*, **18** (1912), 1002.

[2] "Applied Electrochemistry," **52** (1919), 1185.

Temp.	E.M.F.
17°	1·34 volts.
200°	1·25 ,,
500°	1·11 ,,
1000°	0·88 ,,

It is therefore disadvantageous to work at too high a temperature.

(*a*) *Carbon Monoxide Cells.*—The cuprous chloride cell of Borchers need not be considered, because the current obtained was apparently provided at the expense of the copper electrodes, and not by the carbon monoxide. Haber and Moser[1] studied the P.D. obtained between two electrodes of spongy platinum saturated with oxygen and carbon monoxide respectively; the apparatus used is interesting because the electrolyte consisted of a hot glass tube, on the outside and inside of which the platinum masses constituting the two electrodes were deposited. The arrangement is perfectly suitable for measuring the P.D. and, as a matter of fact, the theoretical P.D. was in almost every case obtained. But it is scarcely to be expected that much current could be obtained from a cell of such high internal resistance.

Baur and Ehrenberg[2] applied their device of using molten silver saturated with oxygen as the positive electrode to the study of carbon monoxide cells, and came to the conclusion that nickel could be used instead of platinum as the solid material of a carbon monoxide electrode. A cell consisting of

Nickel saturated with CO	Molten Borax	Molten silver with oxygen

gave 0·75 volts "on balance," but polarised to 0·1 volts when producing a current of 100 milliamps.

The increase in theoretical E.M.F. at low temperatures has already been pointed out. Hofmann and Wurthmann,[3] using a cell with two copper gauze electrodes covered with spongy copper, and saturated with carbon monoxide and oxygen respectively, obtained 0·99 volts at 20° C.; the electrolyte was a caustic soda solution. The copper of the oxygen-saturated electrode becomes superficially converted to active copper oxide. Other forms of oxygen electrode were also used. The P.D. at the carbon monoxide pole is said to be within 0·02 volts of the theoretical value. This arrangement has been criticised by Auerbach[4] who points out, amongst other things, that the cell has the same disadvantage as that of Jacques, namely, that sodium hydroxide is converted to carbonate during the production of current, and has consequently to be regenerated. Consequently, the approximation to the theoretical value of the E.M.F. gives no measure of the true efficiency.

(*b*) *Hydrogen Cells.*—The first cell of the type

$$H_2 \mid O_2$$

was constructed in 1839 by Grove,[5] who used two platinum electrodes saturated respectively with hydrogen and oxygen. Every one who has ever used a hydrogen electrode in the laboratory knows how easily the P.D. changes if an appreciable current is allowed to be produced, owing to the platinum black becoming unsaturated. It is not surprising therefore to find that the early gas cells polarised readily. Mond and Langer,[6] how-

[1] *Zeitsch. Elektrochem.*, **11** (1905), 593.
[2] *Loc. cit.*
[3] *Ber.*, **50** (1918), 1526; **52** (1919), 1185.
[4] *Zeitsch. Elektrochem.*, **25** (1919), 82.
[5] *Phil. Mag.*, **14** (1839), 127.
[6] *Proc. Roy. Soc.*, **46** [A] (1889), 296.

ever, constructed a cell in which a very large electrode area was provided, and special precautions were taken to prevent unsaturation. One form of the apparatus consisted of a cell divided by a porous diaphragm to each side of which was attached a platinum sheet pierced with tiny holes, and covered with platinum black. The pores of the diaphragm were filled with dilute sulphuric acid, and over one platinum electrode was passed hydrogen and over the other oxygen. The E.M.F. obtained, even on "balance," was under 1 volt (although the theoretical E.M.F is 1·23 volts), and when current was generated, the E.M.F. sank considerably.

A cell was constructed which gave a current of over 2 amperes at 0·73 volts; but, since this cell contained 1·3 grams of platinum, it is clear that the capital cost of a battery capable of giving power on a large scale would be utterly prohibitive.

The energy efficiency of the Mond-Langer cell was about 50 per cent. Like most cells employing platinum black, it was liable to suffer from "poisoning" if the gases employed were not pure.

The Mond-Langer cell has been improved by Siegl,[1] in that the platinum black, instead of being supported on thin sheet of the same material, was deposited on small grains of carbon 3 mm. in diameter. Special precautions were adopted for keeping the electrode material saturated with the respective gases. The oxygen-hydrogen cell is stated to have given an E.M.F. of 0·90 volts and to have supplied current at a total cost of only 4d. per kw. hour. Owing to the present scarcity of platinum, however, it is unlikely that a technical solution of the problem can be found in this direction.

Beutner[2] attempted a hydrogen-oxygen cell in which a fused bath (potassium fluoride and sodium chloride) was used. He inserted into this as electrodes, platinum tubes closed at the end by pieces of thin palladium foil. The tubes contained hydrogen and oxygen respectively which diffused continually through the palladium. Evidently, however, the diffusion was too slow to be useful, for although the cell gave 0·9 volts when balanced, the E.M.F. dropped to 0·5 volts when furnishing 1·8 milliamps., and below 0·1 volts when supplying 4 milliamps.

Baur and Ehrenbach[3] employing, as usual, molten silver as the oxygen electrode, found that they could use nickel, copper, or even iron, instead of platinum as the solid material of the hydrogen electrode, the electrolyte being fused borax. The cell gave nearly a volt when balanced, and yielded 0·5 volts when providing a current of 60 milliamps.

The following table is a summary of the semi-direct type of fuel cell:—

(*a*) *Carbon Monoxide Cells.*

Borchers . .	Cu . . .	Cu_2Cl_2 in acid solution kept saturated with CO .	$CuCl_2$ in acid solution kept oxidised by air.	Cu
Haber and Moser	Pt saturated with CO . . .	Warm glass . .	Pt saturated with oxygen.	
Baur and Ehrenbach . .	Ni saturated with CO . . .	Fused borax . .	Molten silver containing oxygen.	
Hofmann and Wurthmann .	Cu saturated with CO . . .	Sodium hydroxide solution . .	Cu saturated with air.	

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[1] *Electrotechnische Zeit.*, 34 (1913), 1317.

[2] *Zeitsch. Elektrochem.*, 17 (1911), 91.

[3] *Loc. cit.*

(b) Hydrogen Cells.

Grove . . .	Pt saturated with H_2 . . .	Dilute sulphuric acid . .	Pt saturated with O_2.
Mond and Langer	Pt black saturated with H_2 .	Dilute sulphuric acid . .	Pt black saturated with O_2.
Beutner . .	Palladium foil saturated with H_2 .	Fused KF+NaCl	Palladium foil saturated with O_2.
Baur and Ehrenbach . .	Nickel saturated with H_2 . .	Fused borax . .	Molten silver containing oxygen.

Type (3*a*).—Where an oxidation and reduction cell is employed, the E.M.F. to be expected will vary with the materials. Probably Jungner[1] was the first to employ this indirect type of fuel cell. He used a cell consisting of two carbon electrodes immersed in warm concentrated sulphuric acid; the chamber is divided into two compartments by a porous partition. There were several varieties of the cell. Generally the cathode consisted of graphite, and air was forced into the cathode compartment; the anode consisted of lumps of carbonaceous matter, the fuel to be employed being generally utilised as electrode material. The sulphuric acid in the cathode chamber contained an oxygen-carrier such as nitric oxide (which no doubt produced nitrosyl-sulphuric acid through combination with the air which was passing through the liquid); the acid in the anode chamber probably became charged with sulphur dioxide, produced by the action of sulphuric acid on the fuel.

In effect, therefore, we have the oxidation-reduction cell,

Graphite.	Nitrosyl sulphuric acid	Sulphur dioxide	Carbon.

The same cell has been studied by Taitelbaum,[2] who has also tested a variety of different oxygen-carriers. Taitelbaum's most promising cells contained hot concentrated sulphuric acid, to which were added salts of some metals that exist in two states of oxidation. Iron, mercury, cerium, thallium, and vanadium, were all used. The metal was kept in a highly oxidised condition in one compartment by the action of air, and in a reduced condition in the other by the action of the fuel. The air was broken up into minute bubbles by means of a Hoffmann "atomiser," and in several cases the fuel also was used in a very fine state of division. Thus a cell of the type:—

$$\text{Carbon} \mid Tl^{\cdot} \mid Tl^{\cdot\cdot\cdot} \mid \text{Carbon}$$

is maintained. Taitelbaum studied the P.D. provided by the two "half-cells" separately, and came to the conclusion that vanadium was the best metal to employ. He employed various fuels (coal, anthracite, wood charcoal, lignite) as well as gases like coal gas, acetylene, etc., and obtained very interesting results. At 200° a cell of the type

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[1] English Patent 15727 of July 11, 1906; German Patent 206273 of October 31, 1907.

[2] *Loc. cit.*

Carbon | $V^{IV.}$ | $V^{V.}$ | Carbon

yields 0·65 volts when balanced, but the E.M.F. drops to 0·20 volts, when the cell yields a current of 100 milliamps. At 250° the equilibrium value is lower (0·53 volts), but the cell polarises less, the E.M.F. being 0·35 volts at 100 milliamps.

Much experimental work on the subject has been done by Nernst,[1] who has aimed at producing an oxidation and reduction cell which would work at 40° to 60° C., and appears to favour titanium, thallium and cerium. He has also suggested the use of chlorine gas, produced (and regenerated) by the Deacon process, as the oxidising agent in certain fuel cells. It may here be mentioned that the production of current by the recombination of the hydrogen and chlorine produced at electrolytic alkali works is a promising field for investigation.

Nernst would seem to be of the opinion that the most important factor in an indirect cell is the velocity with which the fuel will reduce the metal to the lower state of oxidation and the velocity with which the air will oxidise the metal in the other compartment. Unless the reducing and oxidising reactions can keep pace with the production of current, it is clear that the cell will, sooner or later, cease to work, when the materials originally added have become exhausted. Some of the earlier workers did not realise the importance of this point.

As we should prefer to express it, there are three main causes for the drop in the E.M.F. which occurs whenever the external resistance of the circuit is reduced for the purpose of increasing the current:—

1. The fraction of the total E.M.F. which falls over the interior of the cell. This will become serious, when the *internal resistance* of the cell is comparable in magnitude to the external.

2. The *current polarisation*, or alteration in the P.D.'s at the two electrodes from the equilibrium value which occurs *immediately* when the cell is made to furnish a high current. It depends actually on the current density, and can be reduced by giving the electrodes a large surface area. This type of polarisation can, therefore, be called *surface polarisation.*

3. The *time polarisation* which appears only when the cell has been running for some time. This is due to exhaustion of the oxidising and reducing substances caused by the fact that the actions which should replenish them are not sufficiently rapid. We can, of course, increase the rapidity of the reactions by grinding the fuel more finely, or by breaking up the air-stream into finer bubbles or by increasing the concentration of metallic salts used as oxygen carriers; but, when we have reached the effective limit in these ways, we can only combat the polarisation further, by increasing the volume of the electrolyte employed. Therefore, time polarisation can also be called *volume polarisation.*

Now, since *current* or *surface* polarisation can be determined in a moment, most experimenters have noticed it and measured it, obtaining curves connecting with the E.M.F. of the cell with the current density. But the very existence of *time or volume polarisation* has been overlooked by some workers, who did not run their cells long enough to meet with it. Since the capital expense of the cell depends quite as much on its volume as on its electrode area, this latter type of polarisation is equally objectionable. In fact, what is really the main stumbling block to the financial development of the fuel cell is the immense size of the plant which would be needed to supply even one kilowatt of power.

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[1] German Patents 259500 of July 22, 1911; 264026 of June 15, 1912; 265414 of June 15, 1912.

We suggest, therefore, that future investigators on this subject, in forming an estimate of the success of their results, should arrive at the value, not only of

(1) the energy efficiency (calculated from the amount of power obtained from unit mass of fuel), and (2) the surface area of electrode corresponding to one watt of power (calculated from the current density during the run), but also (3) the volume of the cell (including outside regenerating chambers, if any) corresponding to one watt of power.

Type (3*b*).—In a sense, every primary cell belongs to this type; but, the energy efficiency of an ordinary zinc primary cell is very low owing to difficulties in the metallurgy of zinc. Blount estimates the energy output of a primary cell as only 2½ per cent. of the coal energy needed to provide the zinc. There seems to have been no previous attempt to devise some more efficient form of indirect fuel cell with a metal as attackable electrode material. We therefore defer discussion until we come to this type in our own work.

Part II.—New Experimental Work.

Our own experiments, being of a preliminary character, deal rather with isolated parts of the fuel cell problem. We had not reached the stage when the results should have been pieced together in the detailed study of a complete process.

Suitable Electrolytes.—Most of the successful work has in the past been done in fused baths, but unfortunately many of the salts which fuse readily are oxidising agents. We carried out some work to examine other fused baths, which might be useful for fuel cells, and, incidentally, for certain other work we had on hand:—

Carnallite with 30 *per cent. Potassium Chloride* gives a liquid very fluid at red heat, but tends to creep very readily over the side of the crucible. It also loses chlorine, and gradually develops infusible magnesium oxide; it is reconverted to its original fluid form by grinding and heating with ammonium chloride. The mixture is hygroscopic.

"*Phosphate Glass Mixture,*" consisting of

One part sodium pyrophosphate,
Two parts potassium dihydrogen phosphate,

fused together until all the water is evolved, gives a mass, fluid at yellow heat, *which does not creep.* It is rendered more fluid by adding lead oxide, but this addition was not, in the end, employed by us.

Oxidation-reduction Cell with Phosphate Glass.—The liquid glass mixture dissolves most oxides readily, giving, in many cases, coloured glasses. The rate of oxidation and reduction of various metals in the glasses was studied (the reactions being, in many cases, followed by the colour changes, some of which were of extraordinary beauty) with a view to the selection of a mixture of suitable composition for use in an oxidation and reduction cell; glasses containing the following metals were tested, either singly or together:—

Manganese, uranium, vanadium, cerium, chromium, nickel, platinum, copper, and iron.

As an example of the results obtained we quote the changes in the following glass containing ***uranium*** and ***manganese*** :—

Potassium dihydrogen phosphate	20 grs.
Sodium hypophosphate	10 „
Manganese borate	0·5 „
Uranyl nitrate	0·2 „

The fused glass is amethyst in colour, but becomes yet more purple (due to Mn_2O_7) when fully oxidised. On reduction it becomes first yellow (due to UO_3) and then green (due to UO_2). Beads of standard colour and known state of oxidation (obtained by titration) were prepared, so as to give us definite limits to which to work. The purple glass can be reduced by bubbling coal-gas through it in the liquid state. Some of the times recorded for the two stages were :—

Purple to yellow	30 mins.
Yellow to green	30 „

The oxidation is then brought about by means of air :—

Green to yellow	30 mins.
Yellow to purple	95 „

Curiously enough by reducing the glass at a slightly lower temperature, at which the glass is less fluid, and more inclined to "froth," the reduction is much quicker :—

Purple to yellow	3 mins.
Yellow to green	17 „

Many other glasses were tried, in some cases solid fuels (charcoal) were used as a reducing agent. None of the times obtained really seemed as short as we required, but since the manganese-uranium mixture appeared to be suitable in other respects (which many of the other mixtures were not) a semi-direct fuel cell made up with the glass as electrolyte was roughly tested.

A round "London" crucible was divided diametrically with a tile cut to fit the crucible, but not to reach the bottom. The bottom of the crucible was then filled with broken pieces of refractory (actually another "London" crucible), so as to form a sort of porous diaphragm (after Taitelbaum.[1]). The crucible was then filled with the glass mixture, and, by means of pipeclay tubes, air was bubbled through one side and coal gas through the other. The crucible was heated from below. The electrodes consist of platinum foil wrapped round two pieces of pipe. The electrode immersed in the red (oxidised) glass became the positive pole, that immersed in the green (reduced) glass the negative. They were joined to a 340 ohm. voltmeter. The E.M.F. was not—in this particular cell—determined on "balance," but the voltmeter registered 0·25 volts, and dropped slowly to 0·16 volts. It was then sending about ½ milliamp. through the voltmeter; by reducing the external resistance to 3·4 ohms. the E.M.F. dropped to 0·0016 volts, but the current did not noticeably increase. If, however, the electrodes are moved about, the current rises considerably. Apparently, in spite of the apparent fluidity of the glass it is too viscous for cells of the oxidation-reduction type, and the current polarisation was too big to make it worth while to carry the line of research further. In any case, our previous rough experiments on velocity of oxidation and reductions indicate that time-polarisation would prove a considerable difficulty. The "phosphate glass" cell was therefore abandoned.

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[1] *Loc. cit.*

Experiments on Low Temperature Cells. (*Types* 2 *and* 3*a*).—It seemed reasonable that, in the cell,

Nickel covered with Pt black saturated with hydrogen gas.	Sodium hydroxide solution.	Sodium hydroxide containing manganese hydroxide in suspension, through which air is bubbled.	Carbon

nickel would work well as a substratum for the platinum black of a hydrogen electrode in alkaline solution, since the P.D. of hydrogen towards alkali is more negative than that of nickel. The single P.D.'s. of the half-cells were first examined. On testing the nickel-platinum electrode (over which hydrogen is bubbled by means of the common "slotted-hood" arrangement) using the potentiometer method, very irregular results were obtained, which showed that the electrode does not really function as a hydrogen electrode. In addition, in the cathodic half-cell the rate of oxidation of the suspended manganese oxides was far from being as rapid as was desirable.

Preliminary experiments were made on certain cells, suggested by the Edison accumulator, with the intention of regenerating the electrodes periodically by heat treatment in a reducing and oxidising atmosphere respectively.

Fe gauze cage enclosing Fe hydroxides.	dilute NaOH.	Ni gauze cage enclosing Ni hydroxide.

Fe gauze in contact with iron filings.	dilute NaOH.	Ni gauze in contact with Ni hydroxide.

Fe gauze in contact with iron filings.	dilute Na_2CO_3.	Carbon in contact with MnO_2 (Leclanche pot).

The results indicated, however, that—to obtain non-polarising electrodes of high capacity—some special mechanical arrangement was needed for compressing the oxides into their cage or pot. The experiments were deferred until a time when this problem could be dealt with.

Metallic-electrode Cells of Type 3 (*b*).—Although the use of zinc as an attackable electrode is unlikely ever to solve the "fuel cell problem," it appeared possible that a cell in which some more easily reducible and less strongly basic metal is employed as attackable electrode, being smelted back to metallic form by means of fuel (either inside or outside the cell) as fast as it is used up, might prove successful.[1] Our experiments seem, on the whole, to confirm this view.

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[1] Thermo-chemical data indicate that, if carbon can be used as the ultimate source of energy, the metals tin and lead are the most suitable.

The reduction of various mixtures containing tin, for instance

Sodium carbonate	1·3 parts
Sodium stannate	3 „

was studied, and it was found that the treatment with wood charcoal, or gas-coke yielded globules of metallic tin, which in one case contained an appreciable amount of sodium. Subsequently, the addition of potassium bicarbonate was found useful in rendering the mixture more fusible (actually it loses carbon dioxide as soon as it is stirred into the melt). Our object was to add manganese to a mixture of this kind, and then to constitute a cell of the type—

Tin.	Molten bath + fuel	::	Molten bath oxidised by air.	Passive iron.

Fuel would be added to the left-hand side so as to regenerate tin continuously, and air blown over the iron to keep the manganese in a high state of oxidation. We were prevented from testing this cell by the outbreak of war.

Another set of experiments using aqueous solutions were being conducted at the same time which had reached a further stage when the interruption came. It is well-known that the salts of tin and lead are easily hydrolysed, and that the anodic attack of these metals may therefore give rise to an oxide—or at least a highly insoluble basic salt—which might be periodically separated by means of filter, and reduced with fuel to the metallic state, the metal being then used again.

We tried a number of cells of this type, a few being shown below. The carbon, of course, in each case represents the unattacked electrode (cathode).

(A)	Pb	NaHO solution		MnO$_2$ + C (Leclanché Mixture)	C	
(B)	Pb	Na$_2$CO$_3$ solution		MnO$_2$ + C	C	
(C)	Sn	Dil HCl	::	Conc. HNO$_3$	C	
(D)	Sn	Dil HCl	::	dil HNO$_3$	C	
(E)	Sn	HNO$_3$			C	
(F)	Sn	Dil HCl	::	FeCl$_3$ HCl	C	at 20° C.
(G)	Sn	Dil HCl	::	FeCl$_3$ HCl	C	at 80° to 100° C.

One great advantage in these metallic anode cells is that current polarisation at the anode is generally small. In cell (A), for instance, the local anodic P.D. at 0·2 amps. differs by only 0·04 volts from its equilibrium value.

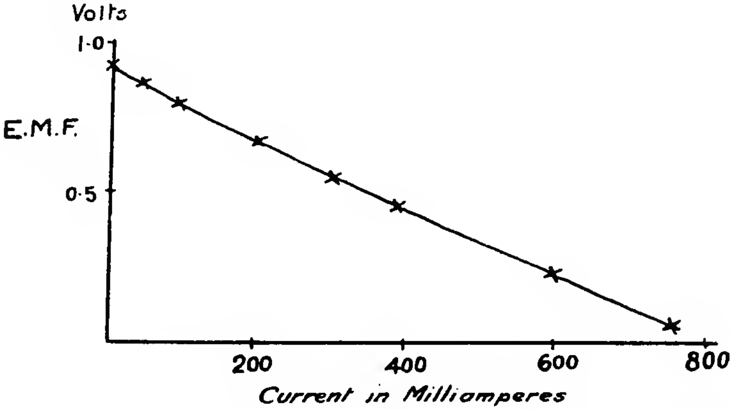
Of these, the lead cells (A and B) gave trouble;

A contained caustic soda which was undesirable;

In B insoluble films were formed upon the lead which obstructed the current, and altered the local P.D. In both cases the regeneration by air of the positive cell (manganese dioxide mixture) appeared to be incomplete.

On the other hand the tin cells seemed much more hopeful. Whether insoluble tin compounds were formed in the liquid or not, there is no obstruction of the current. Those in which nitric acid was used as oxidising depolariser have the possible disadvantage that gases like nitrogen or nitrous oxide may be evolved, which cannot easily be reconverted to nitric acid. This was known to occur in the case of (D), and was suspected in (C). Cell (E) having no porous pot allows local attack of the tin.

(F) was the cell which gave the best results. A cylindrical porous pot was employed; outside it was dilute hydrochloric acid in which the stick of cast tin was immersed; inside the pot was the mixture



Current Polarisation of Cell $Sn | HCl | \frac{FeCl_3}{HCl} | C$

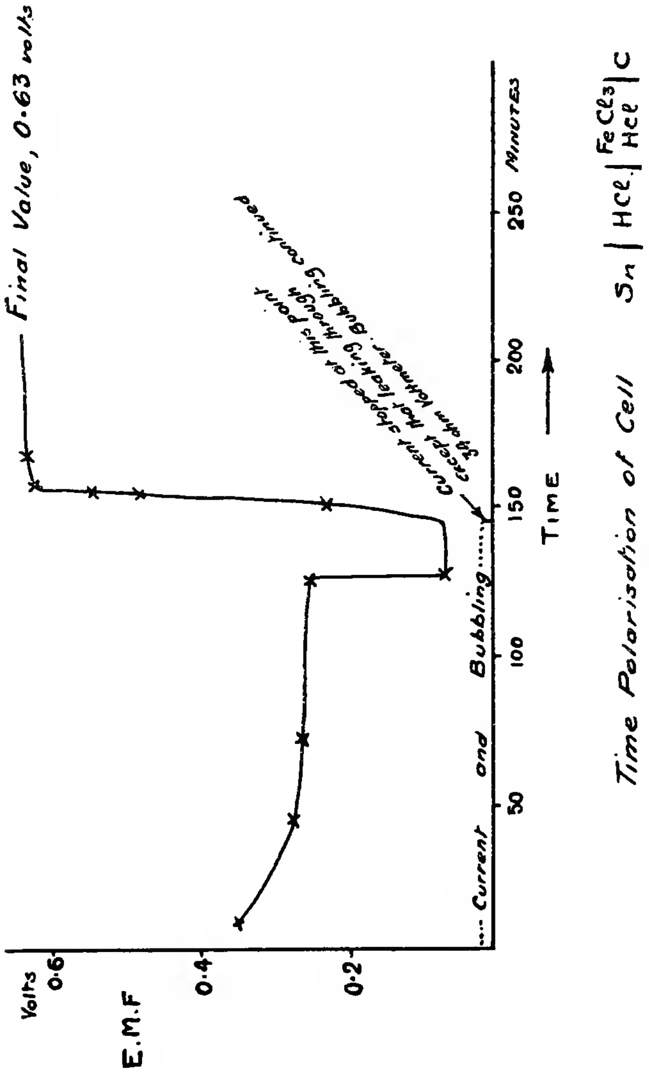
FIG. 2.

"Ferric chloride syrup"	8 c.c.
Water	16 ,,
5 per cent. hydrochloric acid	4 ,,

and a carbon electrode (bichromate battery type) was immersed in it. The immersed areas of the carbon and tin electrodes were 16 sq. cms. and 10 sq. cms. respectively. The volume of the liquid in the inner and outer compartments was 28 c.c. and 80 c.c. respectively at the commencement of the process.

Air was bubbled through the ferric chloride solution continuously. The current polarisation was first tested, the results being plotted in Fig. 2; this is almost entirely due to the positive pole, and considering that no attempt had been made to enhance the surface area by using porous carbon, or packing the jar with pieces of carbon, the effect is not unsatisfactory.

The "time polarisation" was next studied by running the cell at constant external resistance for periods of several hours. It was anticipated that the time polarisation would be serious, since the rate of reoxidation of ferrous chloride by air was known to be not very rapid. Actually it was found that, when the cell was made to generate an approximately constant current of 0·5 amps., the E.M.F. gradually diminished with the time, as shown in Fig. 3, and, finally, when the last trace of ferric salt was used up, it dropped suddenly. The current was then stopped, except that passing



Time Polarisation of Cell $Sn \mid HCl \mid \frac{FeCl_3}{HCl} \mid C$

Fig. 3.

through a 34 ohm. voltmeter, but bubbling was continued. Ferric salt was quickly regenerated and the E.M.F. rises, becoming finally constant at 0·63 volts. Evidently at this point the current sent through the voltmeter (*i.e.* 18 milliamps.) was exactly equivalent to the rate of oxidation by the air-stream. A very similar number, namely 19 milliamps., was arrived at in a separate experiment in which we approached the final value from the other side, by allowing an originally highly charged cell to exhaust itself through a 34 ohm. voltmeter, the E.M.F. finally becoming constant at 0·66 volts. The value (1·8 to 19 milliamps.) may appear very low, but it must be remembered that the volume of liquid was very small (25 c.c.), and that no precaution was taken to break up the air into fine bubbles.

On the whole the results were not discouraging. It was hoped to reduce both types of polarisation by working at 80° to 100°. As a matter of fact, we found that current polarisation was greatly reduced at this higher temperature, and the E.M.F. of the cell was considerably raised. During a two hours' run a current of 0·11 to 0·13 amps. is generated at 0·85 to 1·10 volt. Time polarisation appeared at first to have vanished, the E.M.F. tending rather to rise than to fall with the time. Afterwards, however, complications arose; the liquid lost hydrogen chloride as vapour, and precipitates appear in the ferric chloride solution which did not readily dissolve even when fresh acid was added. It seemed likely that the increased diffusion of the stannous chloride through the pot at the higher temperature was also a cause of trouble. Certainly the first difficulty, and probably the second could have been overcome, if time had been allowed us.

It only remains to say that the "tin hydroxide" precipitate which collected in the positive compartment of the cell after it had been running from time to time, could be filtered off and reduced with coal gas; globules of metallic tin are produced, but there is a difficulty in making them coalesce. It would, of course, not be allowable to employ borax or similar flux, if the tin is to be regenerated completely.

SUMMMARY AND CONCLUSION.—Fuel cells may be classified as—

(1) *Direct fuel-cells* burning solid fuel. These suffer from current polarisation due to the low velocity with which carbon enters into electrodic reactions.

(2) *Semi-direct fuel-cells* burning gaseous fuel. These suffer usually from current polarisation due to the difficulty of keeping the electrode material saturated with gas. Mond and Langer overcame this, but in doing so used so much platinum that their cell became far too expensive for practical use. An attempt by ourselves to use nickel instead of platinum as the substratum of a gas-electrode was unsuccessful.

(3) *Indirect cells* of

(*a*) *Oxidation-reduction Type.*—These suffer from not only (i) *current* polarisation, dependent on the electrode *area*,

but also (ii) *time* polarisation, dependent on the cell *volume.*

This second kind of polarisation is economically most important, but has been overlooked by some workers. Some fresh cells of this type were tested by us, but proved unsuitable.

(*b*) *Metal Anode Type.*—Zinc appears unsuited, but preliminary experiment with different cells (both hot and cold) in which tin was the active element gave results which seemed promising.

Our results are necessarily incomplete, but it is probable that further research on these lines might lead to favourable results. Every future experimenter, however, should state, as a criterion of success (we are unable to do in our own case owing to the unfinished character of our work)—

$$\left.\begin{array}{l}\text{1. The fuel consumption}\\ \text{2. The electrode area}\\ \text{3. The cell volume}\end{array}\right\}\begin{array}{c}\text{corresponding}\\ \text{to}\\ \text{one watt.}\end{array}$$

DISCUSSION.

Mr. W. R. Cooper remarked that the authors, like most others who had worked at this subject, seemed to disregard the fundamental difficulty, namely, that it was desirable to use carbon as an electro-positive element, but that this became impossible because carbon refused to act as an ion in solution. Consequently all sorts of inefficient expedients were attempted, often having no quantitative relation with the output of electricity, and experimenters fell back on gaseous reactions whose speed was low and which consequently restricted the output far below the figure commercially necessary. Under these conditions the carbon was not really the "attackable electrode" as usually understood in the voltaic cell; for such corrosion as occurred was frequently not voltaic.

The authors adopted such a wide classification that it included all cells, which seemed scarcely a useful extension.

Fused electrolytes had received a good deal of attention, but they introduced thermo-electric E.M.Fs., and it was difficult to distinguish these from any voltaic action that might occur. Moreover it was very doubtful if any commercial efficiency could be obtained in this direction, for more energy was likely to be put into the cell than the energy taken out of it.

The distinction between "current polarisation" and "time polarisation" seemed artificial. The latter could also be found in all voltaic cells and was regarded as a sign of overloading. It was more noticeable in the cells considered by the authors, because these were limited in their rate of output much more acutely by the speed of reaction.

To enable the commercial performance to be judged, the size of cell should be stated in all cases, but the authors had omitted data of this kind.

Although he was not sanguine that the authors would achieve success, he hoped they would not be discouraged in their efforts.

Dr. J. A. Harker, F.R.S., said that if it were possible to regard as a cell one in which no liquid electrolyte was present, some experiments which he made along with Dr. G. W. C. Kaye just before the war seemed to have a bearing on the considerations laid before them by Dr. Rideal. In a carbon tube furnace at very high temperature the atmosphere was very highly ionised and in a lecture given at the Royal Institution, the speaker had demonstrated the possibility of constructing an ionic generator of electric currents, based on the electric emissivity of carbon. In one series of experiments he had obtained electro-motive forces up to 3 volts by this method, and currents of several amperes. The early work was all done with electrically heated furnaces and far more energy was being put in in the form of alternating current for heating purposes than was given out as direct current, carried by the streams of negatively charged particles. It was not easy to obtain definite effects without electric heating, but this had been successfully accomplished and there was no doubt of the genuineness of the phenomena described.

The speaker reminded Mr. Cooper that, in the work on the Diesel engine during its development period, many of the early forms of engine required to have the flywheel turned round by means of a strap, and it was only after a lot of experiments that an engine was obtained which ran independently and gave a positive output. Dr. Harker said that he was of opinion that some day it ought to be possible to construct a real cell whose energy was derived from the combustion of carbon and in which electric heating was not employed.

The President asked what was the relationship between the energy put in and the energy got out. Was it of the order of one-tenth per cent. ?

Dr. Harker said that in the actual apparatus, which he showed at the Royal Institution ten years ago, the heating took about 1 kw., and about 10 watts were got out; but that was only a demonstration apparatus and was constructed with no regard to efficiency. It was simply to show the kind of thing it could do.

Mr. U. R. Evans, replying to the discussion, said he was sorry Mr. Cooper did not like the name "time polarisation," but it appeared the best name to express the effect in question; Mr. Cooper seemed to agree, however, that the effect actually existed, and that it was an effect which limited the current obtainable from a cell. The authors thought that the effect had been overlooked by some of the previous workers and that was why they desired to emphasise it in the paper by giving it a special name.

With regard to Dr. Harker's extremely interesting remarks, the fact that, in Dr. Harker's cells, more energy was put in than was got out was not a conclusive argument against the future usefulness of such cells; any process, when worked on a small scale, was highly inefficient, because the losses due to radiation and other causes were immense compared with what they were when the process was worked on a large scale. The same criticism would apply to attempts to carry out the metallurgy of metals on a small scale. Radiation losses depended upon the surface area and as the plant was increased in size the ratio of surface to volume decreased and therefore the proportionate loss of energy decreased also.

HIGH TEMPERATURE PHENOMENA OF TUNGSTEN FILAMENTS.

BY THE RESEARCH STAFF OF THE GENERAL ELECTRIC CO., LONDON.

(Work conducted by C. J. Smithells, B.Sc.)

(*A paper read before* THE FARADAY SOCIETY, *Wednesday, June 22nd,* 1921, PROFESSOR ALFRED W. PORTER, F.R.S., PRESIDENT, *in the Chair.*)

[*Received May 26th,* 1921].

SUMMARY.

Part I.—Two types of tungsten wire are in general use for lamp filaments. One is composed of pure tungsten, and the other of tungsten containing up to 1 per cent. of a refractory oxide such as thoria.

The crystal growth during burning has been investigated for both types. It is shown that the deformation of the filament which occurs during life, is a function of the crystal growth.

Crystal growth, which is suppressed in thoriated filaments, occurs when the thoria is reduced.

Thoria, and other refractory oxides, can be reduced by phosphorus vapour at a high temperature.

Part II.—Deals with the chemical reactions which occur in gas-filled tungsten filament lamps when traces of the common gases are present in the filling gas. The types of failure which are produced in each case are described.

The paper is illustrated by photomicrographs.

INTRODUCTION.

In 1913 Langmuir[1] investigated the cause of blackening in vacuum lamps, and found that in well-made lamps it was due to the volatilisation of the tungsten filament. He showed that by filling the bulb with some inert gas such as nitrogen or argon, the volatilisation is largely suppressed. This made it possible to raise the temperature of the filament, thus increasing the efficiency, without risk of blackening. The efficiency obtained in vacuum lamps is about 0·8 candles per watt, whilst in the larger gas-filled lamps the efficiency approaches 2 candles per watt, owing to the higher temperature of the filament.

The manufacture of these lamps has introduced many new problems, and the causes of failure are essentially different from those found in vacuum lamps. For both types of lamp they may be broadly divided into two types, which are dealt with respectively in Parts I. and II.

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[1] *Proc. Am. Inst. Elec. Eng.*, 1913, Vol. 32, p. 1893.

(i) Failures due to alteration in the crystalline structure of the filament giving rise to brittleness, deformation, etc.

(ii) Failures due to reactions which may occur between the filament and gases existing in the lamp, causing blackening, etc.

For vacuum lamps these have already been investigated somewhat fully. Jefferies[1] has described in detail the conditions for crystal growth, in tungsten, and has shown how alteration in the structure of filaments in vacuum lamps may cause failure.

In gas-filled lamps the filament is subjected to rather different conditions. The temperature of the filament, which is about 2300° K. in a vacuum lamp, is 2500° K. in a gas-filled lamp, and the filament is always of spiral form in order to reduce convection and conduction losses. These conditions put a more severe strain on the filament, and it is clear that filaments which prove satisfactory in vacuum lamps may fail when employed in gas-filled lamps.

Langmuir[2] has described the effects of most of the common gases when they occur in vacuum lamps. In a vacuum lamp the phenomena occur at low pressures, and the possibility of the occurrence of an electric discharge is a vital factor. In gas-filled lamps the pressures are of the order of one atmosphere and all the reactions occurring in the lamp have been found to be of a purely chemical nature, and capable of investigation by chemical and microscopic means.

PART I.

Types of Filament.—There are two types of drawn tungsten wire which have been in general use in incandescent lamps for some years. The first type is a pure tungsten filament containing more than 99·9 per cent. tungsten. The second type is a tungsten filament which contains anything up to about 1 per cent. of a refractory oxide, one of the most common being thoria. It is convenient to refer to the first type as tungsten filaments, and the second type as "thoriated" filaments. The two types of filament are found to have very different properties from a metallographic point of view, and will be considered in detail separately.

Tungsten Filaments.—It is well known that a filament wire before burning has a fibrous structure as a result of being drawn into wire, and the ductility of tungsten wire is due to this structure. If the temperature of the filament is raised to incandescence the long fibres break up into equiaxed crystals and the wire loses its ductility.

At the temperature of the filament in a gas-filled lamp grain growth takes place very rapidly. It has been followed in some detail, by taking a series of similar lamps, and burning them for various periods, from a fraction of a second to several hundred hours, the lamps being then broken open, and sections made of the filaments. Fig. 1 shows a series of photomicrographs of sections taken longitudinally through the spiral in which the rate of grain growth can be followed. Grain growth continues until the diameter of the crystals is about equal to that of the wire. After this no further change takes place in the *average size* of the crystals, but there is strong evidence that the condition is not a stable one, and that the crystal boundaries are in constant motion. The final size is attained by the crystals after the filament has been burning about 15 minutes, but this time will vary with the temperature of the filament. Fig. 1, F, showing a fila-

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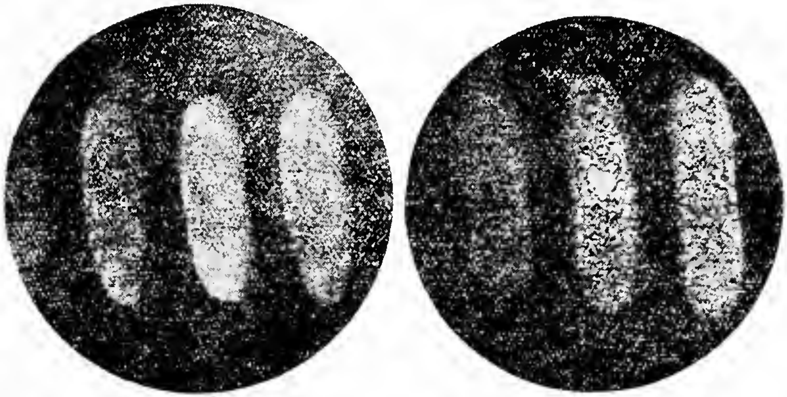
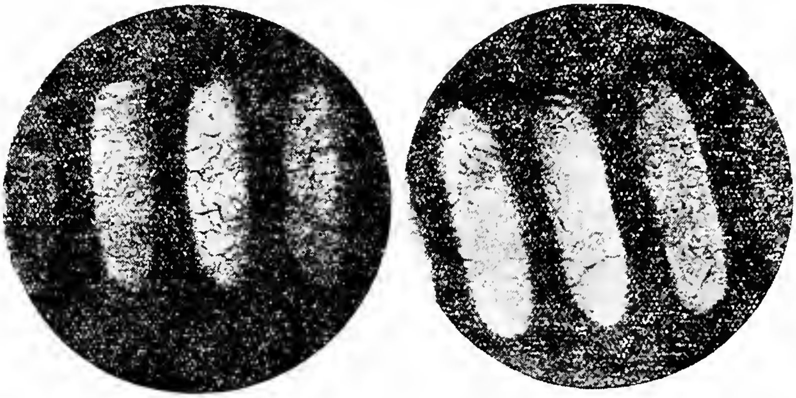
[1] *Bull. Am. Inst. Min. Eng.*, June, 1918, No. 138, p. 1037.

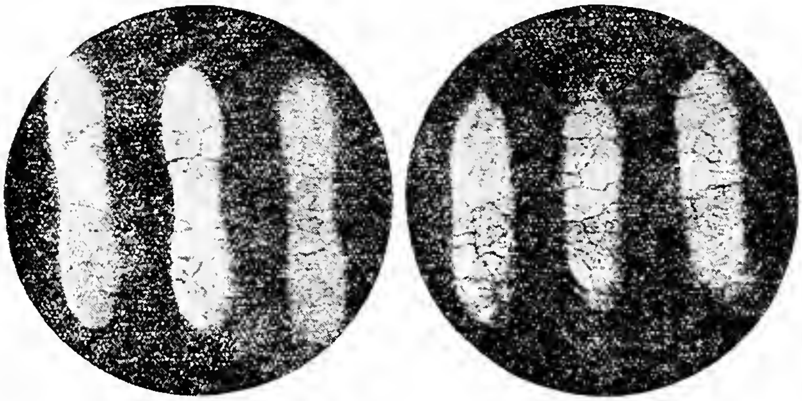
[2] *Loc. cit.*



A, Unburnt. B, ⅕ second.



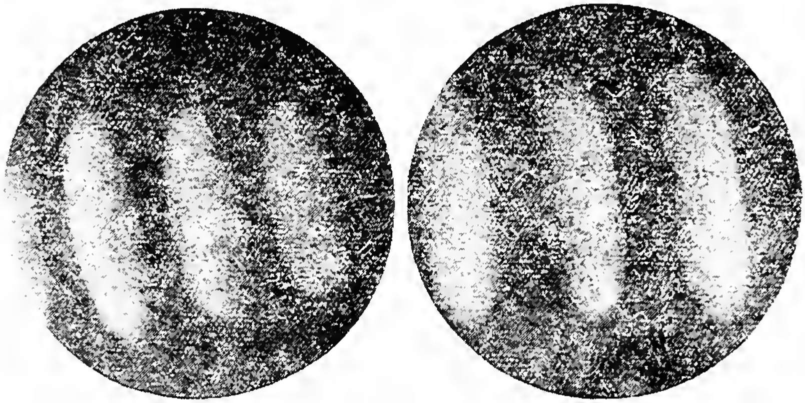
C, 5 seconds. D, 1 minute.



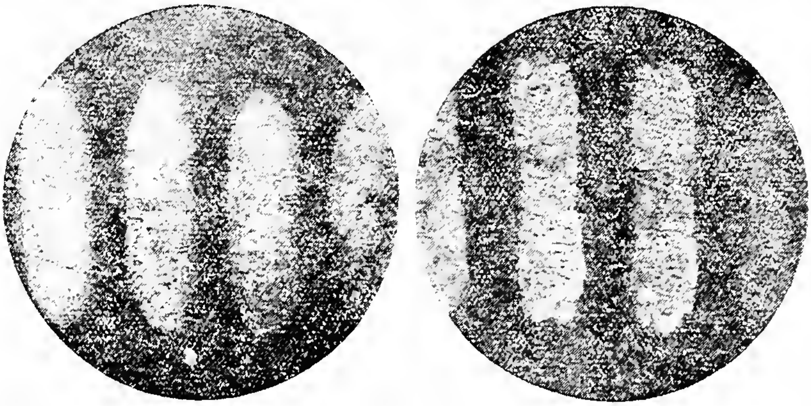
E, 20 hours. F, 600 hours.

FIG. 1.—Etched sections of pure tungsten filaments after various periods of burning at 2500° K. (× 200).
(Reduced by one-fifth.)

ment which has burnt 600 hours, shows the same grain size as that attained after 20 hours (Fig. 1, E), although the outline of the filament has become more angular and crystalline. An examination of the external appearance of the filaments shows that they have deformed under their own weight, and that this deformation has increased with the grain size. It is much more marked during the preliminary period of rapid crystal growth than it is later in life. As in straight filaments, the mechanical strength of the wire is found to decrease with burning, and although strong enough during the early stages, the filaments will not stand severe mechanical shock after the crystal size has become large.



A, Unburnt. B, $\frac{1}{5}$ second.



C, 30 minutes. D, 600 hours.

Fig. 2.—Etched sections of tungsten filaments containing 0·65 per cent. thoria, after various periods of burning at 2500 K (× 200).
(Reduced by one-fifth).

Thoriated Filaments.—In order to retain the tough properties of the fine grained wire it has been customary to add thoria or other insoluble material. There is evidence for supposing that this segregates in the grain boundaries and so restrains crystal growth. The series of photographs in Fig. 2 illustrates the progress of grain growth in a wire containing 0·65 per cent.

of thorium oxide. It is seen that the filament is composed of relatively small grains even after 600 hours' burning. Although the ductility of the wire has been destroyed by equiaxing, the fine-grained structure is exceedingly tough, and these filaments will withstand considerable mechanical shock without breaking, even after 600 hours' burning. These filaments deform very little and what deformation there is occurs gradually during their life.

From comparison of crystal size and the amount of deformation in a very large number of thoriated and tungsten filaments it appears that deformation of the spiral only takes place when there is crystal growth, and that the deformation is proportional to the amount of growth. That is to say—

(i) Permanent deformation of a metal may take place when the stress is actually below the elastic limit for that temperature.

(ii) That such deformation takes place during the movement of the crystal boundaries.

The rapid deformation during the first period of burning of a tungsten filament is due to the rapid growth during that time. Although the average grain size does not subsequently alter, the slow increase in deformation leads to the assumption that the crystals continue to grow at one another's expense during the succeeding hours of burning.

Effect of Reducing Agents on Crystal Growth.—The process of crystal growth described in the previous paragraphs are those which occur normally in thoriated and tungsten filaments. In general, tungsten filaments rapidly grow a coarse crystalline structure, whilst thoriated filaments remain comparatively fine grained, and are consequently stronger. It is found in certain circumstances, however, that the thoriated filaments may behave abnormally and develop a coarse structure like pure tungsten and possess corresponding brittleness. This structure is found to develop, for instance, in those lamps into which red phosphorus has been introduced, this being a common practice in lamp manufacture in order to remove traces of oxidising gases which might attack the filament. The same effect can be produced by the introduction of sodium vapour into the bulb.

Both phosphorus and sodium vapour are active reducing agents, and it appeared probable that the refractory oxide which should have restrained crystal growth in the wire, might have been attacked.

In order to determine if this was the case lamps were made and known quantities of red phosphorus introduced by exhausting the lamp and connecting it to a tube containing yellow phosphorus, until the full vapour pressure had been established. The filament was then flashed, and the phosphorus vapour thrown down as red phosphorus on the bulb and glass stem. When the lamp was subsequently burned the phosphorus gradually vaporised. From the size of the bulb and the vapour pressure of yellow phosphorus at room temperature, the weight of phosphorus thrown down by each "flash" was found. A series of 60-watt lamps were made containing various quantities of phosphorus introduced into them by this method. The lamps were burnt 24 hours, the filaments removed and examined microscopically, and the average grain size of each determined.

The results are given in the diagram, Fig. 3. The introduction of the first 0·01 mg. of phosphorus produces no effect on the filament, and it is in fact oxidised by gaseous impurities in the lamp, left after exhausting. The addition of more phosphorus, however, is seen to result in an increase in the grain size of the filament. This continues until 0·04 mg. of phosphorus have been added, after which no further increase in grain size occurs.

A corresponding series of lamps using a tungsten filament was made up, and the results are shown in the dotted curve of Fig. 3. A comparison of these two series shows that—

(i) The grain size obtained with a thoriated filament and excess of phosphorus, has the same value as that obtained with pure tungsten.

(ii) That phosphorus has no effect on the pure tungsten filaments.

The phosphorus reduces the thoria, and the oxide of phosphorus volatilises. The metallic thorium which remains does not restrain grain growth, which then proceeds as in a pure tungsten filament. That the thoria had actually been reduced was proved by dissolving the filament in a mixture of HF and HNO_3 in a Pt dish. A thoriated filament leaves a white residue of insoluble thoria, whereas a similar filament after burning in phosphorus vapour leaves no residue of oxide, although thorium can be detected by the usual tests. The time required for the reduction to be complete was found to be about 4 hours. The quantity of phosphorus required for complete reduction, as shown by the curve in Fig. 3, is

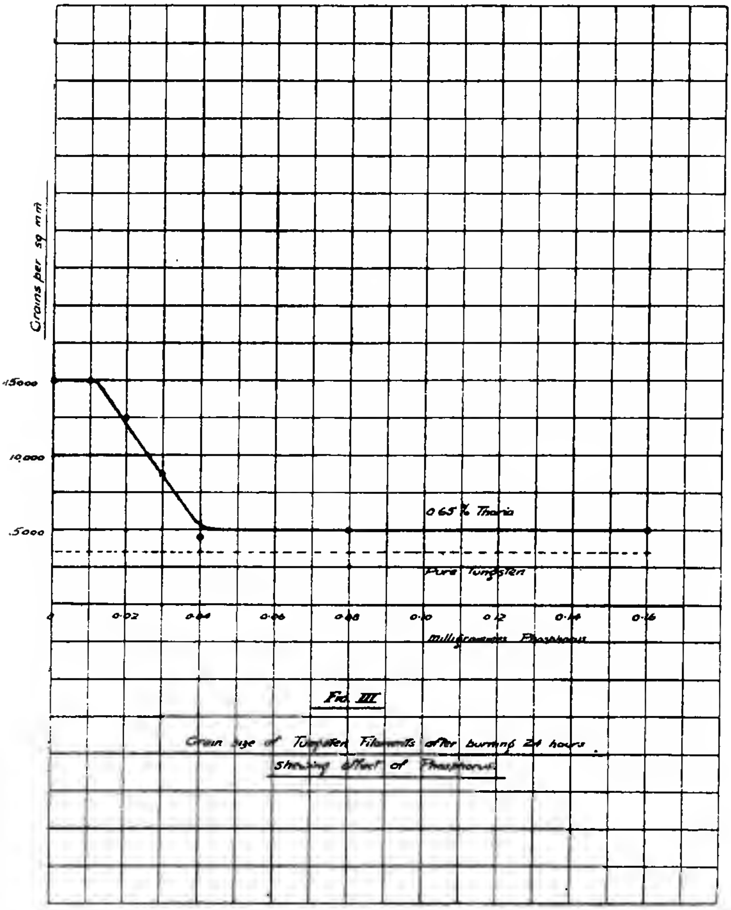


FIG. 3.

0·03 mg. This agrees well with the calculated quantity 0·02 mg. for these particular filaments, assuming that the phosphorus is oxidised to P_2O_3.

Experiments, in which metallic sodium vapour was employed instead of phosphorus, gave similar results, but the reduction took a longer time. Other metallic oxides have been introduced into the wire instead of thoria, and it is found that these are reduced by both phosphorus and sodium in a similar manner.

PART II.

General.—A very common form of failure in gas-filled lamps is accompanied by blackening of the bulb. The filament at the same time is attacked and ultimately fails. The deposit was generally considered to be tungsten or an oxide of the metal, and some impurity in the filling gas was presumed to be the most likely cause. An investigation into the phenomena attending this led to a careful study of the effect upon the incandescent filament of small quantities of the various common gases, introduced into the lamp with the inert gases. Some interesting reactions have been observed, and will be considered in detail.

Oxygen.—Oxygen in relatively large quantities, say 1 mm. pressure, rapidly attacks the filament. Clouds of the yellow oxide WO_3 are evolved from the burning filament and deposited on the bulb. The deposit, owing to its fine state of sub-division, often appears white. With lower pressures of the gas the colour and composition of the deposit alter progressively. In a series of lamps with decreasing pressures of oxygen, the colour of the deposit changes from white to a light blue. With small traces of oxygen the deposit is the lower oxide, W_2O_3, which is dark blue. The intermediate colours represent mixtures of these two and possibly intermediate oxides.

The brownish-black oxide, WO_2, does not appear to be formed by direct combination with oxygen at any pressure.

Hydrogen.—Hydrogen does not react with hot tungsten, and lamps have been made containing 5 or 10 per cent. of hydrogen in the gas. This in no way diminished the life, or changed the appearance of the lamp.

Water Vapour.—This is one of the most interesting gases in connection with lamp manufacture, and one of the most difficult to eliminate. Langmuir[1] describes the effect of water vapour in a vacuum lamp, and shows that the tungsten oxide, which is formed by reaction with the hot filament, is reduced again by the hydrogen at the cold walls of the bulb. This results in a transference of tungsten from the filament to the bulb.

If a trace of water vapour is introduced into a gas-filled lamp and the filament burnt in a projection apparatus, it is observed that the turns of the spiral in contact with the supporting wires, and therefore relatively cold, gradually become thicker. At the same time one or two turns on either side of this point become thinner, until it is ultimately eaten through, and the lamp fails. This thickening of the spiral at the coldest spots, and thinning at adjacent points of higher temperature occurs at all the supports, or at any point where a temperature gradient exists. It should be noted that the part which thins is not the hottest part of the filament, although the hot parts of the filament may be slightly attacked, but is some point on the temperature gradient. The appearance of the filament at the point where it was in contact with a supporting wire is shown in the photographs in Fig. 4. A shows the filament, and the five thick turns in the centre are clearly seen, with thin turns on either side. B is an etched section of the same specimen. C is another filament showing where failure has occurred at the thinned part. D is a section of the same specimen.

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[1] *Loc. cit.*

The reaction which takes place is represented by the reversible equation

$$W + nH_2O \rightleftarrows WOn + nH_2.$$

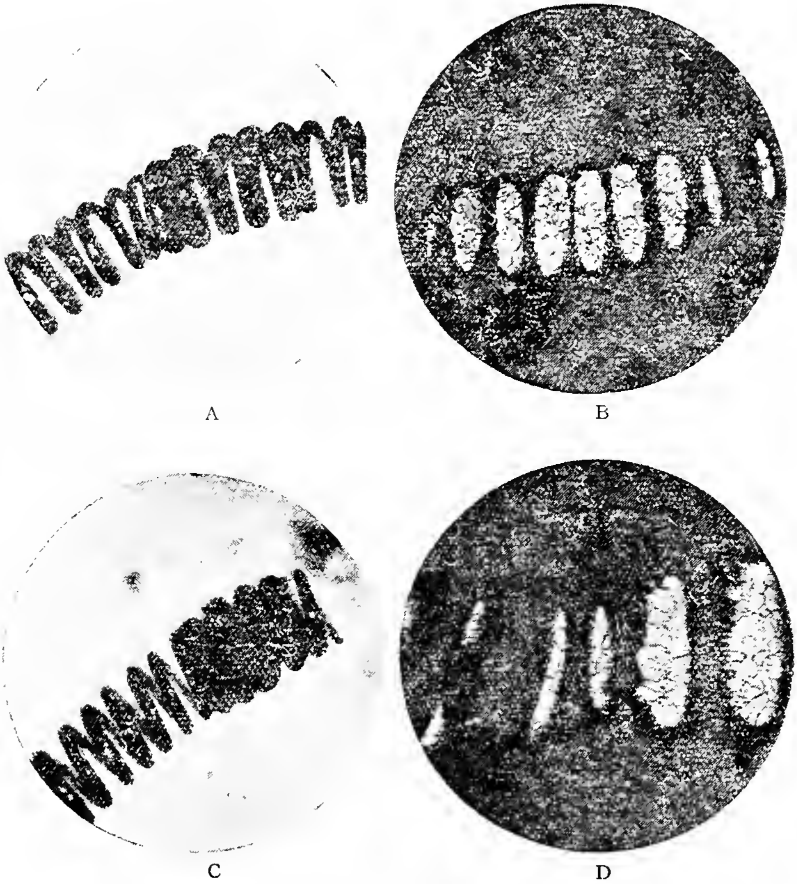

FIG. 4.—Tungsten filaments showing the action of water vapour.
B is an etched section of A.
D is an etched section of C.
A, B and C (× 100); D (× 150).
(Reduced by one-fifth.)

The equilibrium condition requires a higher concentration of the oxide at the higher temperature. The oxide formed at the higher temperature being carried past the cold part in contact with the support, is largely reduced by the hydrogen, and tungsten is deposited on the cold turns of the spiral, where it is incorporated in the existing crystals. This is clearly seen in Fig. 4, D, where the original crystal grains are no longer discernible, having increased as fresh tungsten was deposited. A certain proportion of the oxide as well as some reduced metal is carried past the cold portion of the filament and forms a brownish-black deposit on the bulb.

Owing to this cyclic action a very small quantity of water vapour introduced into the lamp with the argon, or evolved from the glass walls, has a very destructive effect on the lamp.

If only a small quantity of water vapour is present it may require several hundred hours for the filament to fail, but with larger quantities the reaction proceeds sufficiently fast to be readily observed when suitable magnification is employed.

Carbon Dioxide.—This gas attacks the hottest parts of the filament and forms a light blue oxide, similar in appearance to that obtained with a trace of oxygen. It is probable that carbon is deposited with it, but it is masked by the oxide. If, instead of introducing the carbon dioxide before burning the lamp, the gas is slowly admitted to the lamp during burning, a lower oxide is deposited which is dark blue, appearing brown by transmitted light.

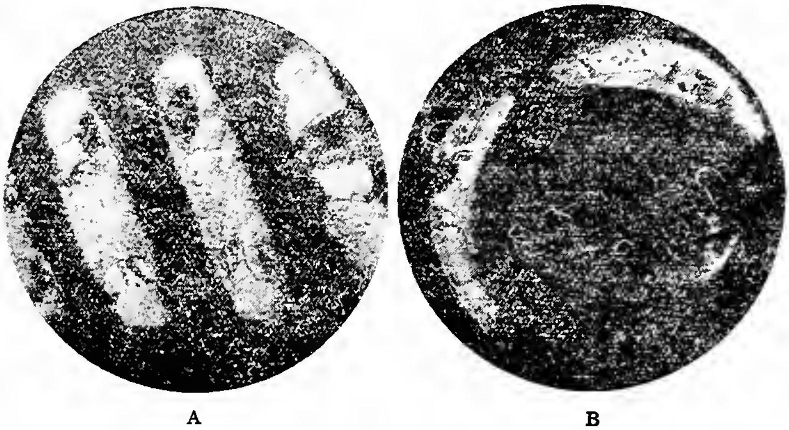

FIG. 5.—Unetched sections of tungsten filaments showing carbide produced by the action of hydrocarbons.
(Reduced by one-fifth.)

Carbon Monoxide.—Carbon monoxide is very slowly broken up by an incandescent tungsten filament. A lamp filled to atmospheric pressure with the pure gas will burn for 24 hours and only show a slight blackening. The gas is probably broken down to carbon and carbon dioxide. The former is deposited, and the latter, being always present at low concentration, produces the dark oxide as described in the last paragraph. The attack and failure take place at the hottest parts of the filament, and the result is thereby distinguishable from the action of water vapour, where failure occurs near the supports.

Hydrocarbons.—The action of hydrocarbons on a hot tungsten filament is very vigorous. If a hydrocarbon vapour, such as naphtha, is passed over the spiral filament of a gas-filled lamp the filament immediately begins to twist and squirm, and very soon breaks up. It is found to be exceedingly brittle and micro examination shows that the whole surface of the spiral has been attacked. The appearance is shown in Fig. 5. A shows a longitudinal and B a transverse section through the spiral. The surface is converted into tungsten carbide, which is exceedingly hard and stands out white on the etched specimen. The same effect is produced by methane, or hydrocarbon vapours from molten paraffin wax.

Carbon Monoxide and Nitrogen.—As has been mentioned elsewhere in this paper, metallic sodium vapour was introduced into lamps in order to test its effect on the crystal growth of the filament. The presence of the sodium also gives rise to another interesting reaction, although it has no detrimental effect on the lamp. It is found that a greyish white deposit is formed on the glass stem in the lamp, and on analysis this is found to contain sodium cyanide. The argon used in the lamp always contains a certain percentage of nitrogen and small quantities of carbon monoxide are continually being evolved from the surface of the hot bulb.

H. v. Wartenburg [1] has pointed out that in an electric arc between carbon electrodes in an atmosphere of nitrogen, an intense cyanogen spectrum can be seen. According to Nernst's theorem the following percentages of CN should exist in equilibrium with C and N at the temperatures given.

Temp. °K.	Per Cent. CN.
2300	0·01
2800	0·9
3300	17·0

Cyanogen has not, however, been isolated by this method, as it is decomposed reversibly as it cools.

When sodium vapour is present, the cyanogen formed at the surface of the hot filament combines to form sodium cyanide. This is carried by convection currents in the lamp and deposited on the stem.

The reaction is probably complex. The oxygen of the carbon monoxide also combines with the sodium and gives sodium oxide, which has been detected. The final result is, however, shown by the equation

$$3Na + CO + N = NaCN + Na_2O.$$

The rate of formation of sodium cyanide increases very rapidly with increasing temperature of the filament. Although less than 1 per cent. of cyanogen is required by theory for equilibrium at 2500° K., owing to its removal as fast as it is formed, the amount produced is quite considerable.

In a 60-watt lamp running at normal temperature, and through which was passed a current of CO, N and sodium vapour, 0·5 gm. of NaCN was formed in 100 hours.

The filament takes no part in the reaction, being merely necessary to raise the temperature of the reacting gases.

DISCUSSION.

Mr. Fonda (of the General Electric Co. of America) said that the question of the reduction of thoria in the thoriated filament in the presence of phosphorus was a very interesting point indeed, and should lead naturally, as the author had said, to the formation of an alloy between the reduced thoria and the tungsten. He wondered if the author had made any observations of the electrical resistivity or temperature coefficient of the resistance, which in that case should show a change from the value previously found for the thoriated filament, in which the oxide present might be called an adulterant, and would therefore have no effect upon the temperature coefficient of the pure metal tungsten.

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[1] *Zeit. anorg. Chem.*, 52, 599, 7907.

Mr. W. B. Clarke (Edison & Swan Electric Co., Ltd.) said that there were one or two points upon which he would like to ask Major Smithells for further information. The paper had not referred to the so-called single-crystal tungsten filament, about which a great deal was said some time ago in the technical papers, and which, he believed, was the subject of two or three patent applications. The filament was manufactured and heat-treated in such a way that the filament up to 50 or 60 inches in length consisted of one single crystal. Another question was that not long ago a new form of filament called the Non-Sag filament was introduced, and, he believed, was the subject of a patent by the General Electric Co. of America, in which niobium was mentioned as being introduced in the filament, which had the effect of making the tungsten filament much stronger at high temperatures and prevented it from sagging. That was a question which, perhaps, the author could enlighten them upon. The question also arose, with regard to the crystallisation of tungsten filaments, as to the form of current used. In the early days of electric lamp manufacture it was believed and, in fact, was proved almost beyond dispute, especially with the earlier types of lamp using osmium and tantalum, that alternating current had a greater effect on crystal growth than direct current. In fact, it was no uncommon thing to see a filament in the form of a series of stalactites $\frac{1}{16}$th or $\frac{1}{32}$nd of an inch long all joined together in the form of a long series of cylinders forming a zig-zag known as off-setting, and, seeing that the frequency of the alternating current also had a great effect, he would like to know whether the experiments in the paper were carried out with alternating or direct current, and if with the former, the frequency of the supply. With regard to etching, there were many ways of etching tungsten, but it was a difficult problem at its best, and he would like to know what method was used for etching the sections shown in the author's slides.

Again, there was the question of the effect of hydrocarbon vapour on the filaments, which brought into consideration whether the use of oil pumps was advisable in the manufacture of incandescent lamps, seeing that, however carefully treated, some hydrocarbon vapour, even if only in infinitesimal amounts, was bound to get into the lamp, and it was these small amounts of impurities which were the bugbear of lamp manufacture. No mention was made in the paper of mercury vapour. There were some tungsten lamps which were supposed to work in mercury vapour, and some information as to the effect of mercury vapour, if any, on crystal growth in tungsten filaments would be valuable.

Dr. H. Borns asked whether he had correctly understood Major Smithells to say that the amount of water vapour used in the experiment on the break-down of the filament must be very small, otherwise the failure would only take place after 600 hours or so. The author had also spoken of introducing sodium; was that sodium introduced in the metallic condition?

Major Smithells: Yes.

Dr. H. Borns continuing said that the author would be acquainted with the experiments of Hamburger, who coated filaments with silicates and found that metallic sodium was then liberated, but that sodium was not liberated from caustic soda. Although Mr. Paterson had come down upon questions about crystal growth, he would like to ask whether they had confirmed the experiments made in the Pintsch works, that a tungsten wire, passed through a coil of incandescent tungsten, developed crystals feet in length.

Dr. E. Fyleman, dealing with the question of crystal growth, said that as it was well known that large crystals grew at the expense of small ones, there seemed no very obvious reason, beyond the possible presence of oxide or other impurity in the filament, why the large crystal, once started in any filament, should not extend throughout the whole length of it under such conditions as those referred to in the paper. He suggested that possibly the reason why that did not happen was that the ·05 per cent. of oxide which was present just spread itself to the extent of the so-called maximum size of the crystal, but could not then get any further, and they perhaps had a film of oxide of possibly molecular size which spread itself until the two phases were in approximate equilibrium. It followed from the experiments referred to in the paper that the oxide would have to be an oxide of something that was not reduced by phosphorus, otherwise both the thoriated filament and the non-thoriated filament would become mono-crystalline; but they did not.

Dr. D. Hanson said he thought the argument that large crystals grew at the expense of small crystals was not accurate, because it had been indisputably shown by Dr. Carpenter and Miss Elam that large metal crystals did not necessarily grow at the expense of small ones. Indeed, it was quite often the case that the small ones grew at the expense of the large ones.

Dr. Fyleman: They do not in this case.

The President asked Mr. Hanson if the suggestion was that the small crystals grew until they were of an equal size.

Mr. Hanson replied that a position of equilibrium arose, but there was no definite rule on the question of whether the large crystal grew at the expense of the small one, or *vice versa*.

The President said that the problem of the formation of these crystals was undoubtedly one of the most interesting points in connection with filaments, and he was afraid that the question of single crystals was one which must inevitably come into the discussion. He would very much like to hear what theory of the growth of crystal size was favoured by the author. He believed it was true that the only reason why small crystals formed at all instead of a single crystal was the presence of an impurity of one kind or another. Further, when crystals are obtained, what made them grow at high temperatures? Was it a question of evaporation from the small crystals to the big one—he would not have it the other way round—or was it a question of solution taking place of the intersticial material which prevented a single crystal being formed to start with? He did not know whether any evidence had been accumulated as to what the process was which took place generally. It must be exceedingly difficult to arrive by experiment at a definite conclusion. In the case that had been brought before them that evening a *succession* of filaments had been examined. It had not been the same filament in different stages of growth, and the fact that there did not seem to be any obvious way of examining the filament as it grew made it very difficult to put forward any safe theory as to what really happened while crystal growth was going on. However, the fact that crystal growth did take place was proved, and it was a most interesting and important fact technically.

Major Smithells, replying to the discussion, said it was very difficult to say, in reply to Mr. Fonda, whether the resistance changed owing to the reduction of the thoria or not, because the resistance of the filament depended more than anything else on its temperature. As the filament burned it changed its shape, the turns became spread out and the temperautre varied, and the change in resistance of the filament did not represent the influence of reduction. The temperature coefficient had to be taken account of. He had tried taking the resistance of filaments of different types under different conditions, but in this particular case, where the reduction of the thoria might alter the resistance, the results were abortive, because the effects he was looking for were much smaller than the variations owing to change of temperature.

With regard to offsetting, mentioned by Mr. Clarke—the crystal grains growing out in all directions—that was well known to occur with alternating current in the vacuum lamp. With the spiral filament, however, he had had no sign of offsetting. One of the slides showing the filament after 600 hours burning showed a very rough surface, but there was nothing in the way of failure due to offsetting. The experiments were nearly all done on alternating current, but no difference was observed between alternating current and direct current from that point of view. Whether that was due to the spiral form of the filament he did not know, but he presumed it must be so, as similar filaments in a different form showed offsetting. As to etching, there was no secret about the method. The filament was mounted on a small brass base with a groove in it, and some powdered lead borate put in. The whole thing was heated up until the brass was hot enough to melt the lead borate. The piece of filament was then allowed to sink into the lead borate which was afterwards polished down. The period of etching varied up to one minute in boiling hydrogen peroxide, and that gave perfectly satisfactory results. Boiling in sodium picrate gave a better contrast, but it was not quite so clean or simple to use. As to mercury vapour, he had made up lamps containing globules of mercury, but that had had no effect. In the vacuum lamp it had a great effect, because the heavy molecules were shot about and did damage, but in the case of the gas-filled lamp mercury vapour was quite harmless. Oil pumps were used by most people in pumping lamps, but the amount of oil vapour obtained, if a good oil were used, did not cause trouble.

He had been asked whether the cyanide process had been taken up commercially. As a matter of fact, he wasted a few weeks trying to make something of it, in the hope that he would find a new way for the fixation of nitrogen, but the result was abortive. He believed a patent had been obtained in America or here, he was not sure where, which produced the same effect in a simpler manner by the use of molten iron, but he did not believe that the new reaction was likely to prove practicable. The figures for the temperature coefficient for the amount of cyanide formed at the different temperatures were in the paper. The curve was a very steep one, and it was seen that a small alteration in the temperature of the filament would result in a large alteration in the amount of cyanide formed, but he did not think it was practicable to maintain tungsten at a temperature near its melting-point for any length of time, which would be necessary for a commercial process of this kind.

Dr. Borns must have misunderstood him with regard to the amount of water vapour in the lamp which he exhibited. What he meant to say was that a small quantity would produce failure in perhaps a minute, whilst a quantity not very much different from that small quantity might take 600 hours, the difficulty being to get just exactly the right small quantity in the lamp. Sodium vapour was always introduced by passing a current of inert gas over molten sodium. Sodium had a very appreciable vapour pressure when it was molten, and generally he put it in a bath of lead or something of that sort and just passed the gas over it, and the sodium vapour went through.

The question of crystal growth was a most interesting one, and a great deal had been done on the question of the crystal growth of other metals besides tungsten. Tungsten was supposed to have peculiar properties, but it was really due to the position of the melting-point. If other metals were treated at the temperature of liquid air the same results were obtained as when tungsten was treated at ordinary temperatures, but the crystal growth in tungsten and other metals was similar. He believed that Dr. Fyleman's theory of a film of oxide could hardly hold, for several reasons. For instance, in the case of pure copper exactly the same phenomena were obtained.

Dr. Fyleman: How do you know you can get copper pure?

Major Smithells replied that at any rate it could be got much purer than tungsten. Another thing that went against the oxide theory was that all the oxides tried were easily reduced by phosphorus. He believed that thoria was quite as refractory to reduction as most of the other oxides which were likely to occur. There were oxides like silica, which might not be reduced, but there was quite a lot of evidence that a great many of these oxides were absorbed by the tungsten and did not interfere with grain growth. They were not all pushed forward to the crystal boundary as the crystal grew; a lot of them were left behind in the tungsten. He did not think that theory could definitely be ruled out, but what he personally knew about it was that in the case of ordinary pure tungsten it reached a definite equilibrium with regard to grain size after a certain time. He accepted the correction made by Mr. Hanson as to the result of the work of Dr. Carpenter and Miss Elam, but whatever it was that made one grain different from the other, when they had reached a certain average size they appeared for some reason to have a more or less equal power of growth against each other, with the result that nothing appreciable happened. Possibly, if they had a filament with unlimited temperature, there would, at a given temperature, be certain grains which would grow differently from others, but as far as he could understand it, the rate of growth when the different crystals got to a certain uniform size was so small that in practice, at any rate, they did not go any further. That was hardly an explanation, but there was no doubt that when there was the greatest contrast in the grain size there was the more rapid growth. The more nearly they were the same size, the less did they appear to eat each other. The question of getting a long crystal had been given a good deal of attention, but it was too big a subject to deal with that evening, and must be left for future discussion. The actual cause of crystal growth in the first instance was that as soon as cold-worked metal, that had been highly strained, got to the annealing temperature, the grains began to eat each other, so as to get rid of the strain existing in the metal. That, however, was not unique to tungsten; it was simply the ordinary annealing process.

A SIMPLE METHOD OF DETERMINING THE COAGULATION VELOCITY OF GOLD SOLS.

By Emil Hatschek.

(*A paper read before* The Faraday Society, *Wednesday, June* 22, 1921, Professor Alfred W. Porter, F.R.S., President, *in the Chair.*)

[*Received May* 26*th*, 1921.]

The published methods of determining the coagulation velocities of sols fall under three heads: (1) analytical determination of the concentration of disperse phase at various stages of the process (Paine); (2) viscosity measurements (Freundlich and collaborators); and (3) ultra-microscopic count of the particles at various stages (Zsigmondy and collaborators). The first method is applicable in special cases only and does not appear to have found extensive use. As regards the second, it is confined to sols in which coagulation is accompanied by measurable changes in viscosity, *i.e.*, practically to hydroxide and similar sols, and it suffers from the defect that, in the present state of our knowledge, there is no known quantitative relation between viscosity and number or volume of particles. The third method is no doubt the most satisfactory one, but involves the possession of a slit ultra-microscope and considerable skill in using it.

The method to be described consists in determining the percentage of blue formed in the coagulating red gold sol by direct comparison with a double wedge, one half being formed by the original red sol and the other by the same sol completely coagulated, *i.e.*, blue. The simple apparatus used is illustrated in Fig. 1.[1] A rectangular cell, the two sides AA of which are glass plates, while the ends and bottom are ebonite or other inert opaque material, is divided by an oblique thin glass partition B. One half of the cell is filled with the red gold sol to be examined and the other with the completely coagulated blue sol, the latter being stabilised by the addition of a few drops of gelatin or gelatose sol. This cell is placed between two guides CC mounted on a base plate, and a second cell exactly like it placed immediately on top of it. This cell does not require a partition except for the purpose of providing the same optical thickness. The sol which is to be examined is mixed with a known volume of electrolyte—the time of adding the latter being noted—in a beaker and then charged into the upper cell. The two fields, one of which varies from 100 per cent. red to 100 per cent. blue, while the other gradually changes from red through violet to blue, are matched through a slit E about 2 mm. wide in a black screen D (omitted in the elevation, where the slit E is shown in dotted lines). By adjusting the slit so that the tints in the upper half (the coagulating sol) and in the lower (standard red and blue) match, the percentage of blue formed can be read off directly on a scale placed on the base of the triangle of which the partition B is the hypotenuse.

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[1] Since the above was written I have found that a similar arrangement has been used for matching solutions containing indicators (N. Bjerrum, Die Theorie der alkalimetrischen u. azidimetrischen Titriermethoden, Chem. tech. Vorträge, 21 1/3 H. 1914).

Matching is most conveniently done by placing the slit at definite points on the scale and noting the time when the two fields match, as this avoids fatigue. The best illumination is diffuse light from a bright sky; a thin screen of matt glass behind the apparatus generally improves the conditions. The excess of red in most artificial light is such as to make matching by it much less accurate than by diffuse daylight. With the latter matching can be carried out with considerable accuracy, and with concordant results, by different observers. As the slit is 2 mm. wide and the scale in the apparatus used by the author 80 mm. long, the accuracy obtainable is within $2\frac{1}{2}$ per cent., which is probably greater than the accuracy possible in matching.

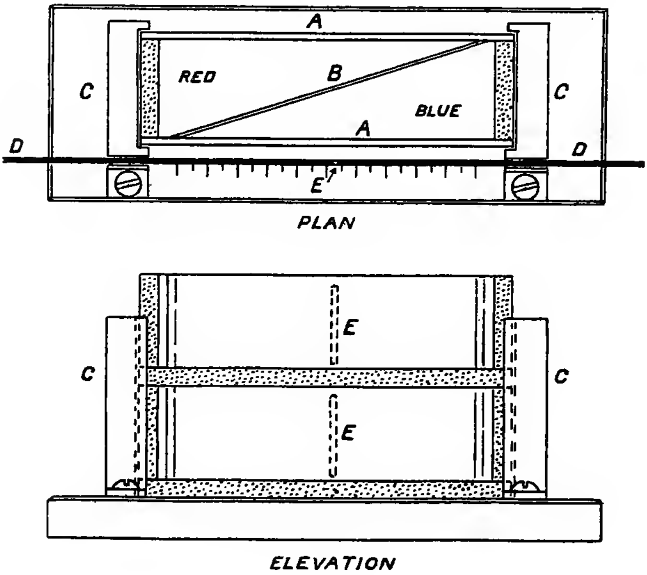

Fig. 1.

In the first trials with the apparatus the blue comparison sol was made by rapid coagulation, generally with acid. In trying to determine the coagulation velocity of sols coagulated with other electrolytes great difficulty was experienced in matching at any point of the scale, owing to a great difference in *depth or intensity*, as distinct from *percentage composition*, of tint. It was, however, found that accurate matching became easy, if the blue comparison sol was coagulated with the same electrolyte, and at something like the same rate, as the sol to be examined.

A number of determinations were carried out, two sets being illustrated in Figs. 2 and 3. The gold sol used throughout was reduced by dextrin, a method described originally by Lüppo-Cramer,[1] and so modified by the author that only the quantity just necessary for reduction is used, no excess of dextrin being left for protection. The sol can easily be prepared in batches of about 300 c.c. as follows: 0·06 gm. of white dextrin is dissolved in 300 c.c. of water, 2 c.c. of N/1 NaOH and 3 c.c. of 1 per cent. solution of $HAuCl_4 . 4H_2O$ or $NaAuCl_4 . 2H_2O$ are added and the mixture heated slowly. It turns a purple pink which gradually deepens and between 95° and 100° changes to a deep ruby red without a purple tinge. The sol is very stable and shows normal, but not excessive sensitiveness to electrolytes.

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[1] *Photog. Corresp.*, 1909, p. 528.

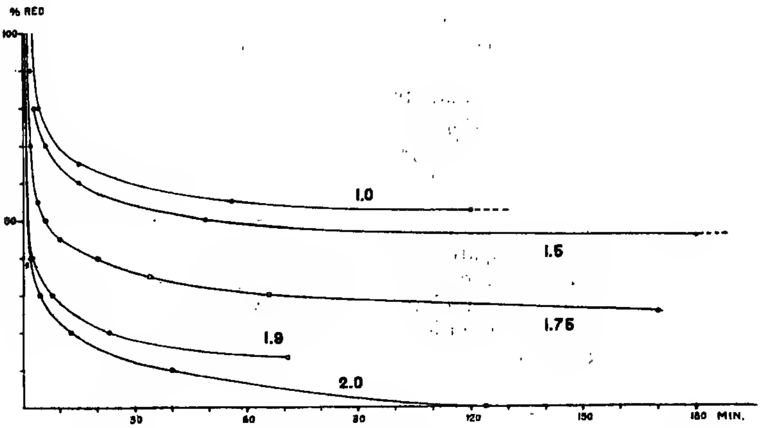

FIG. 2.

In the series illustrated in Fig. 2 the blue comparison sol was made by coagulating 60 c.c. of the standard sol with 2 c.c. of M/10 $CaCl_2$. (The half cell only holds 30 c.c., but the quantity required to fill the whole cell was used, so as to keep the conditions of mixing, etc., exactly alike.) The colour change was complete in about two hours, at the end of which time the blue sol was stabilised by the addition of 0·5 c.c. of gelatose, made by boiling a 10 per cent. sol of washed gelatin for 24 hours with reflux condenser. 60 c.c. batches of the sol were coagulated with the volumes

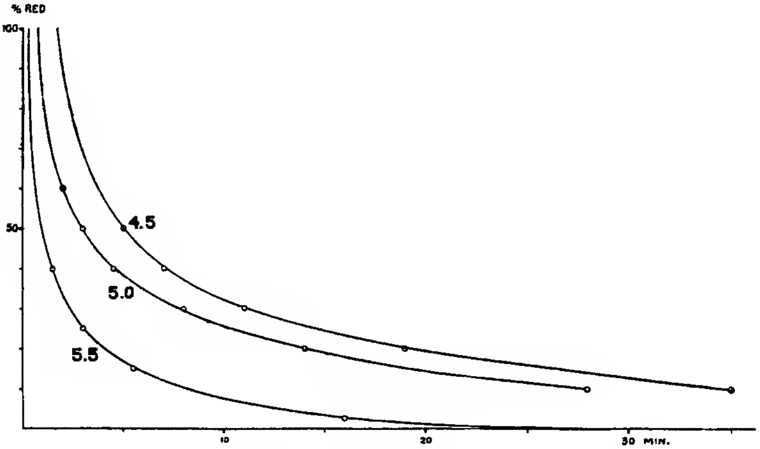

FIG. 3.

of M/10 $CaCl_2$ noted on the curves, water being added to bring the total volume to that of the blue comparison sol, *viz.*, 62·5 c.c. The red comparison sol in the half cell was of course diluted in the same ratio throughout. The latent period before a perceptible colour change occurs is very short, and could be estimated roughly only with the lowest electrolyte concentration. In the other cases it is extrapolated back from the first reading obtainable with certainty. Where the curves are continued in dotted line at the lower end this indicates that the reading was verified after 5 to 12 hours, *i.e.*, that the colour reached remained constant after that period. All the coagulations with less than 2 c.c. of electrolyte are therefore incomplete. The point is of interest, as the difference between 85 and 95 per cent. of blue would be likely to be overlooked without exact comparison.

Fig. 3 shows a set of determinations with HCl as coagulating electrolyte. In this case the blue comparison sol was made by adding 6 c.c. of N/10 hydrochloric acid to 60 c.c. of sol and stabilising with 0·5 c.c. of gelatose after 30 minutes. The coagulation velocities were determined for three different electrolyte concentrations, *viz.*, 5·5 c.c., 5·0 c.c., and 4·5 c.c. of N/10 HCl to 60 c.c. of sol. The volumes were of course made up to 66·5 c.c.

Coagulation in this set of experiments more nearly approaches the "rapid" type than in the set illustrated in Fig. 2, and it is therefore of interest to examine how the results agree with v. Smoluchowski's formula.[1] If n is the number of primary particles in unit volume of the original sol, n_t the number of such particles remaining after the time t, counted from the moment of adding the coagulant, this formula reads :—

$$n_t = \frac{n}{(1 + \beta t)^2}$$

where β is a function of the time T required to reduce the number of primary particles to one quarter of the initial number and therefore a constant for any one case.

The only way in which the formula can be applied to the present results is by assuming that the red of the original sol is caused exclusively by primary particles, and that the percentage of red at any stage of the coagulation is simply proportional to the number of primary particles still left in the coagulating sol. In these terms therefore $n = 100$, while n_t = percentage of red at the time t. We therefore obtain for β the value

$$\beta = \frac{10/\sqrt{n_t} - 1}{t}$$

which should be a constant, if the formula holds. The values of n_t, t and β calculated therefrom are tabulated below :—

60 c.c. of sol. + 5·0 c.c. of N/10 HCl.			60 c.c. of sol. + 5·5 c.c. of N/10 HCl		
t.	n_t.	β.	t.	n_t.	β.
2·0	60	0·145	1·5	40	0·380
3·0	50	0·138	3·0	25	0·333
4·5	40	0·130	5·5	15	0·287
8·0	30	0·103	16·0	5	0·280
14·0	20	0·088			
28·0	10	0·077			

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[1] *Koll.-Zeitschr.*, 21, 98, 1917, see also R. Zsigmondy, *Kolloidchemie*, III. Auflage, pp. 70, 71.

In the first series the extreme values of β are in the ratio 2 : 1, which is almost exactly the degree of constancy obtained by Zsigmondy (*loc. cit.*) in testing v. Smoluchowski's formula. In the second series, which more closely approaches the "rapid" and complete type of coagulation, the ratio of the extreme values is 9·5 : 7, a highly satisfactory degree of constancy.

It therefore appears that the assumption made, *viz.*, that the percentage of red is directly proportional to the number of primary particles—an assumption somewhat difficult to prove on mere *a priori* grounds—is correct. The further tacit assumption that a simple additive law holds for the mixture red—blue in the coagulating mixture seems also to be justified by the results.

It is also of interest to examine how far the results conform to the rule established by Paine for the coagulation of $Cu(OH)_2$ sols. According to him the times t and t' required by sols containing different concentrations of coagulating electrolyte c and c' to reach the same stage of coagulation, *i.e.*, the same n in the present notation, are in constant ratio :—

$$t/t' = (c'/c)^a$$

where the exponent a is 5-6 for univalent ions. This relation is tested in the following table, where the values of t' for n_t = 30, 20 and 10 have been determined by interpolation on the curve shown in Fig. 3 :—

	5·0 c.c. of N/10 HCl in 66·5 c.c. total (c = 7·52 millim.)	5·5 c.c. of N/10 HCl in 66·5 c.c. total) (c' = 8·27 millim.)	
n.	t.	t'.	t/t'.
40	4·5	1·5	3·0
30	8·0	2·5	3·2
20	14·0	4·0	3·5
10	28·0	8·2	3·4
		Mean value	3·27

From the formula given above we obtain :—

$$\log 3{\cdot}27 = a\,(\log c' - \log c) \div a = 12{\cdot}4.$$

While the constancy of the ratio t/t' is satisfactory, the value of the exponent is twice as high as that found by Paine for univalent ions. This is probably merely an instance of the abnormal effect if H ion; it may be added that a concentration of about 50 millimoles of NaCl is required to produce the same effect as about 10 millimoles of HCl, and the results with cations of normal mobility like Na would probably lead to much lower values of the exponent.

The discussion of the results obtained seems to show that the method used gives results comparable in accuracy with those obtained by the existing ones, while there can be no doubt of its very much greater simplicity. The latter makes it suitable for students' use, and a small expenditure of time should give them an insight into the mechanism of coagulation and particularly of incomplete coagulation, a subject on which most text-books are somewhat reticent.

In conclusion one point, briefly referred to already, deserves further mention. The author has confirmed the observation that identical sols coagulated "completely" (the criterion being complete sedimentation after 12 hours) by different electrolytes have not by any means the same colour. Since he understands that this difference is being investigated in Prof. Svedberg's laboratory he has not thought it necessary to devote further attention to it at the moment.

THE INFLUENCE OF THE SOLVENT UPON IONISATION AND THE ACCOMPANYING HEAT EFFECT.

BY SIDNEY MAURICE NEALE.

(Communicated by Professor W. C. M. Lewis.)

(*A paper read before* THE FARADAY SOCIETY, *Wednesday, June* 22, 1921, PROFESSOR ALFRED W. PORTER, F.R.S., PRESIDENT, *in the Chair.*)

[*Received June 6th*, 1921.]

The present paper deals with the degree of ionisation of picric and of *p*-nitro-benzoic acids in mixtures of acetone and water.

The electrical conductivity method is employed, and the degree of ionisation is calculated from the results in the usual manner.

As the effect of the solvent upon the degree of ionisation is in general very marked, one would expect to find an effect upon the heat of ionisation. Such a change in the heat of ionisation would imply that the internal energies of either reactants or resultants, or both, vary with the solvent, *i.e.* are not dependent upon temperature alone.

Walden,[1] working with potassium and tetra-ethylammonium iodides in three organic solvents, concludes that the heat of ionisation of a given electrolyte, is, in general, independent of the nature of the solvent. On the other hand, Dutoit and Duperthuis[2] conclude that the heat of ionisation of sodium iodide has not the same value in different solvents. They attribute the variations in the heat effect to solvation of the ions or of the undissociated molecules.

Smits[3] shows on a thermodynamic basis that when the summation of the entropy terms of the reactants is the same in different solvents, *i.e.* when the influence of the solvent is of a physical nature only, then the difference in position of equilibrium is to be referred to a difference in the heats of dissolution of the components in the various solvents.

Godlewski[4] determined the ionisation of moderately strong acids in mixtures of alcohol and water by conductivity measurements, and showed that the Dilution Law of Ostwald was applicable in all cases studied. The ionisation constants obtained by this author showed a rapid decrease as the alcohol concentration increased. Since his measurements were only carried out at a single temperature, we cannot draw from them any conclusion as to the heat effect involved.

It seemed desirable, therefore, to determine experimentally the heats of ionisation of some electrolytes as a function of the composition of the solvent.

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[1] *Zeit. phys. Chem.*, **59**, 192 (1907).

[2] *J. Chim. Phys.*, **6**, 699 (1908).

[3] *Proc. Acad. Sci. Amsterdam*, **19**, 708 (1917).

[4] *J. Chim. Phys.*, **3**, 393 (1905).

EXPERIMENTAL.

Conductivity water was prepared in the usual manner. The conductivity of the water so obtained varied between $0{\cdot}5 \times 10^{-6}$ and $1{\cdot}0 \times 10^{-6}$ reciprocal ohms. Pure dry acetone was obtained by allowing A.R. acetone (from British Drug Houses) to stand for several days over fused calcium chloride, then distilled over bright metallic calcium through a twelve pear still-head. The product passed over within 0·1° C. and had the specific conductivity $3 - 5 \times 10^{-7}$ reciprocal ohms. The mixtures of acetone and water were made up by volume at 15° C., thus 70·52 weight per cent. acetone was prepared by mixing 750 c.c. of pure acetone with 250 c.c. of conductivity water.

The method of Kohlrausch was employed for the determination of resistance with a metre wire bridge and extension coils, each coil of exactly 4·5 times the resistance of the bridge wire; giving an effective bridge length of ten metres. The cells used were of the Arrhenius closed type, of borosilicate glass, with rigidly supported electrodes. The cell constants were determined at 25° and 35° by means of $\frac{N}{50}$, $\frac{N}{100}$ and $\frac{N}{1000}$ KCl.

While measuring the conductivity of an approximately 25 per cent. acetone solvent, it was noticed that the resistance fell rapidly with time, but showed a momentary rise on gently shaking the cell. This effect was observed in a cell with rather heavily platinised electrodes, and was found to decrease as the amount of platinisation decreased, being absent when polished electrodes were used. The rise in conductivity was therefore attributed to the catalytic action of the platinum black on the aqueous acetone, giving rise to an electrolyte, probably acetic acid.

Owing to this effect it was therefore desirable to work with unplatinised electrodes throughout, but this was impracticable with solutions of specific conductivity greater than 5×10^{-4} reciprocal ohms., since polarisation caused a marked lack of sharpness in the mimimum. A compromise was effected by using polished electrodes as far as possible, and very slightly platinised electrodes at higher concentrations of electrolyte. In all cases care was taken to see that the readings were independent of time, at any rate over several hours.

The picric acid used was 99·8 per cent. pure, and melted sharply at 122° C.

The strongest solution was made up by weight and the others were prepared by dilution.

The thermostats were maintained at 25° and 35° C., with an accuracy of 0°·05. The resistance of each solution was determined first at 25°, then at 35° and then again at 25°.

The values for the heat of ionisation were calculated from the equation:—

$$\frac{d \log K}{dT} = \frac{\text{heat absorbed}}{RT^2}$$

where K is the Ostwald constant, *i.e.* $\frac{\alpha^2}{(1 - \alpha)v}$.

The integrated form of this equation, *viz.*:—

$$\text{heat absorbed} = \frac{2{\cdot}303 \, . \, R \, . \, T_1T_2}{T_2 - T_1} \log_{10} \frac{K_2}{K_1}$$

was found to give in all cases results practically identical with those calculated by Walden's method.[1] For dilutions at which the degree of ionisation exceeds about 97 per cent. the value of the heat effect is not calculated, as a small error in α causes a large variation in Q.

(1) Picric Acid in Water.

Values corrected for specific conductivity of water, namely:—

$1·0 \times 10^{-6}$ mhos. at 25°, $1·2 \times 10^{-6}$ mhos. at 35°.

Dilution in Litres.	$\lambda_{25°}$.	$\lambda_{35°}$.	$\alpha_{25°}$.	$\alpha_{35°}$.	$K_{25°}$.	$K_{35°}$.	Heat Evolved in Calories.
32	343·5	388·1	·913	·906	·299	·273	4610
64	354·0	401·0	·941	·937	·234	·216	4570
128	362·1	411·1	·963	·960	·196	·180	4580
256	368·0	418·3	·979	·977	·174	·162	4510
512	372·1	422·7	·989	·987	·174	·147	—
1024	374·1	424·7	·994	·992	·176	·120	—
1280	374·4	425·2	·995	·993	·155	·110	—
5120	375·3	427·0	·998	·997	—	—	—
∞	376·1	428·2	—	—	—	—	—

The above values of λ agree fairly well with those of H. Gorke,[2] and of Rothmund and Drucker.[3]

The values of α agree well with those given by Jones and Jacobson[4] and also with those of Smith and Jones.[5]

The mean value for the heat of ionisation of picric acid in water at 30° C., is 4570 calories evolved.

As regards the estimation of λ_∞ several numerical values were employed and the corresponding equilibrium constants calculated. The value of λ_∞ adopted was that which gave a regular curve for the variation of K with dilution.

(2) Picric Acid in 70·52 Per Cent. (By Weight) Aqueous Acetone.

Values corrected for specific conductivity of solvent, namely:—

$1·5 \times 10^{-6}$ mhos. at 25°, $2·0 \times 10^{-6}$ mhos. at 35°.

Dilution in Litres.	$\lambda_{25°}$.	$\lambda_{35°}$.	$\alpha_{25°}$.	$\alpha_{35°}$.	$K_{25°}$.	$K_{35°}$.	Heat Evolved in Calories.
32	87·8	101·7	·821	·814	·117	·111	1090
64	93·4	107·8	·873	·862	·094	·085	1890
128	98·0	113·5	·916	·908	·078	·070	1940
256	101·6	118·1	·949	·945	·069	·063	1900
512	104·5	122·0	·976	·976	·077	·077	—
1024	105·4	123·2	·985	·985	·063	·063	—
2048	106·3	124·2	·994	·994	·075	·075	—
∞	107·0	125·0	—	—	—	—	—

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[1] *Zeit. phys. Chem.*, **59**, 192 (1907).

[2] *Ibid.*, **61**, 500 (1908).

[3] *Ibid.*, **46**, 827 (1903).

[4] *Amer. Chem. J.*, **40**, 397 (1908).

[5] *Ibid.*, **50**, 33 (1913).

λ_∞ was determined as in the previous case. In both cases the values are close to the greatest λ values actually observed.

(3) Picric Acid in 87·76 Per Cent. Aqueous Acetone.

Values corrected for specific conductivity of solvent, namely:—

$1·2 \times 10^{-6}$ mhos at 25° C.; $1·4 \times 10^{-6}$ mhos at 35° C.

Dilution in Litres.	λ_{25°.	λ_{35°.	a_{25°.	a_{35°.	K_{25°.	K_{35°.	Heat Evolved in Calories
8	36·95	37·60	·336	·298	·0213	·0158	5390
16	47·60	48·51	·433	·384	·0206	·0149	5920
32	58·50	60·67	·532	·481	·0189	·0139	5590
64	69·38	73·09	·631	·579	·0168	·0125	5460
128	79·36	85·03	·722	·674	·0146	·0110	5210
256	87·57	95·70	·796	·758	·0121	·0093	4868
512	93·9	104·4	·854	·827	·0097	·0077	(4190)
1024	99·8	111·7	·907	·885	·0086	·0067	4790
2048	104·2	117·6	·947	·932	·0083	·0061	5560
∞	110·0	126·2					

Mean value for heat of ionisation

5330 calories evolved.

Figures in parenthesis were omitted in the calculation of the mean value. In this case the determination of λ_∞ is more difficult, as the acid is much less ionised than in the previous solvent mixtures. A good approximation may be obtained by the Washburn method for calculating λ_∞.[1] This method assumes that in the case of strong electrolytes the Ostwald constant approaches a limit with decreasing concentration. It consists in calculating the equilibrium constants for various arbitrary values of λ_∞, plotting the values of K against concentration, and rejecting those values of λ_∞ which cause the curve to exhibit radical changes in direction. Washburn applied the method to very strong electrolytes, such as potassium chloride and to dilutions of the order 10,000 litres, but picric acid in 87·76 per cent. acetone is a very much "weaker" electrolyte, and therefore the method may presumably be applied at greater concentrations. The variation of K with assumed values of λ_∞ is shown in Fig. 1.

The values of λ_∞ thus obtained are 110 at 25° and 126·2 at 35°. The limiting values of K are about 0·008 at 25° and 0·006 at 35°, compared with Washburn's value 0·02 for strong electrolytes in water.

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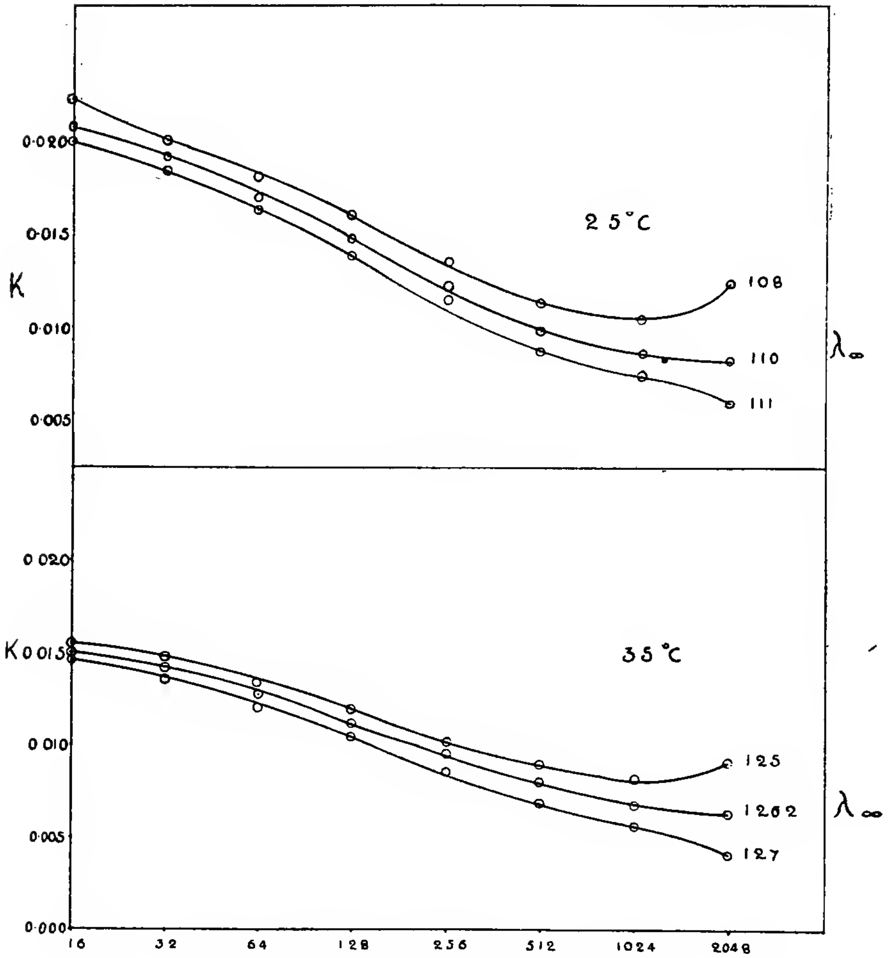
[1] *J. Amer. Chem. Soc.*, **40**, 128 (1918).

Ostwald constants for picric acid in 87·76 per cent. acetone (aqueous).



Dilution in litres (scale of log V).

FIG. 1.

(4) PICRIC ACID IN 93·80 PER CENT. ACETONE.

Values corrected for specific conductivity of solvent, namely:—

1·0 × 10^{-6} mhos. at 25°, 1·2 × 10^{-6} mhos. at 35° C.

Dilution in Litres.	$\lambda_{25°}$.	$\lambda_{35°}$.	$\alpha_{25°}$.	$\alpha_{35°}$.	$K_{25°}$.	$K_{35°}$.
4	11·51	10·80	·0894	·0730	·00219	·00140
8	17·42	16·04	·1297	·1084	·00263	·00165
16	24·95	22·98	·1937	·1552	·00290	·00178
32	33·31	30·81	·2646	·2082	·00278	·00171
64	44·13	41·31	·3426	·2790	·00278	·00169
128	54·96	53·01	·4277	·3580	·00249	·00156
256	68·26	66·65	·5310	·4503	·00235	·00144
512	81·9	82·2	·637	·5554	·00219	·00136
1024	93·9	96·9	·731	·6546	·00193	·00121
2048	105·0	111·5	·817	·753	·00178	·00112
4096	114·0	123·7	·887	·8355	·00169	·00104
∞	128·5	148·0	—	—	—	—

The values of λ_∞ were obtained by the Washburn graphical method, *cf.* Fig. 2.

For dilutions between 4 and 16 it will be seen that K increases with dilution, that is to say, we have an anomaly in the opposite sense to the anomaly of strong electrolytes. This anomaly cannot be removed or diminished to any great extent by substituting other values for λ_∞. It seems probable that there is association of the picric acid molecules at the higher concentrations, such association naturally diminishing the number of ions and hence the value of K, to such an extent, as to outweigh the ordinary increase in K with increasing concentration.

Calculating the heat of ionisation as before, from the values of K at corresponding dilutions, we have:—

Dilution.	$K_{25°}$.	$K_{35°}$.	Heat Evolved.
4	·00219	·00140	(8120)
8	·00263	·00165	(8520)
16	·00290	·00178	(8920)
32	·00278	·00171	(8880)
64	·00278	·00169	(9090)
128	·00249	·00156	8550
256	·00235	·00144	8960
512	·00219	·00136	8700
1024	·00193	·00121	8530
2048	·00178	·00112	8470
4096	·00169	·00104	8870

Omitting the values in parenthesis, owing to the abnormal trend of the K values, we have the mean heat of ionisation = 8680 calories evolved.

Ostwald constants for picric acid in 93·80 per cent. aqueous acetone.

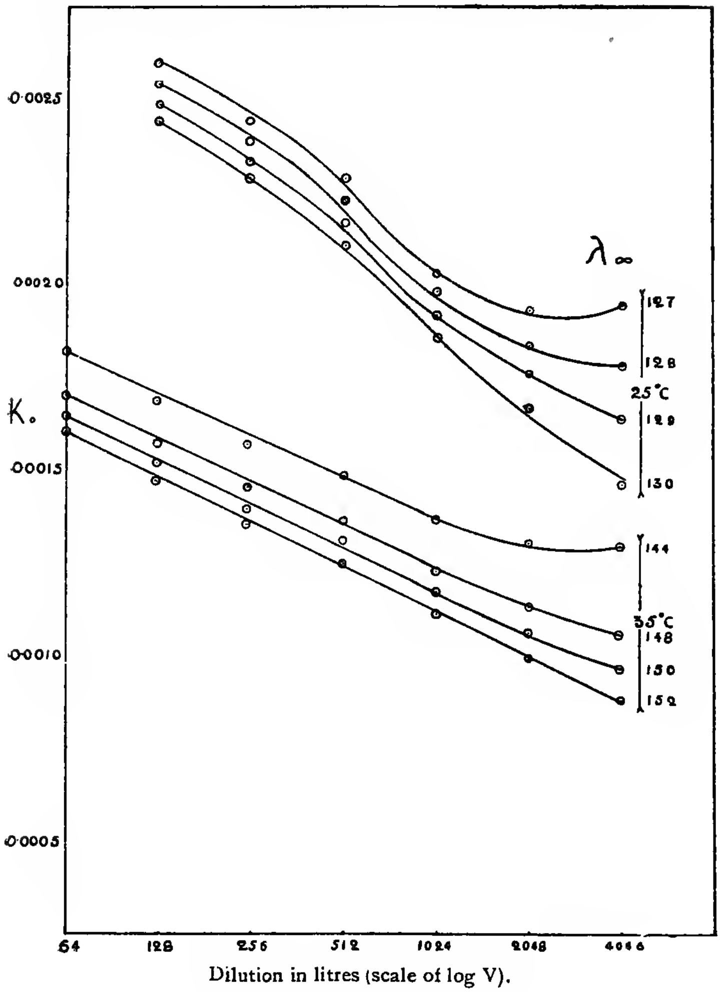


FIG. 2.

(5) PICRIC ACID IN PURE ACETONE.

Values corrected for conductivity of solvent, namely :—

0·3 × 10^{-6} mhos at 25°, 0·4 × 10^{-6} mhos at 35°.

Dilution in Litres.	$\lambda_{25°}$.	$\lambda_{35°}$.
4	·311	·283
8	·458	·411
16	·645	·572
32	·909	·810
64	1·26	1·12
128	1·77	1·58
256	2·59	2·42
384	3·11	2·91
1024	4·64	4·52

To calculate ionisation constants from these figures, it was, of course, necessary to know the values of λ_∞ at the two temperatures. Owing to the weakness of picric acid in acetone extrapolation by any of the methods employed above was impossible. Since the values of λ observed are in all cases small compared with λ_∞, an error in λ_∞ will not largely affect the constancy or otherwise of the Ostwald constant K ; nor will small errors in the values of λ_∞ appreciably affect the heats of ionisation calculated, so long as the ratio of the values of λ_∞ calculated for the two temperatures is almost identical with the ratio of the true values.

The Walden empirical rule λ_∞ = constant, give for picric acid in acetone the value $\lambda_\infty = 1128$ at 25° C. This rule, however, seems inapplicable to acetone solutions.[1]

In the case of inorganic salts Laszozynski's approximation states that λ_∞ in acetone is 1·3 times λ_∞ in water. This gives for picric acid $\lambda_\infty = 500$. Such relations are, however, of very doubtful applicability where the hydrogen ion is concerned.

A more reliable value for λ_∞ may probably be obtained by extrapolating the values of λ_∞ calculated for 0·0 per cent., 70·52 per cent., 87·76 per cent., 93·80 per cent. acetone to 100 per cent. acetone. Compare Fig. 3.

This method gives for λ_∞ at 25° the value 150 and at 35° the value 173.

With the aid of these values we may calculate the degrees of ionisation, the Ostwald constant, and hence the heat of ionisation.

PICRIC ACID IN PURE ACETONE.

Dilution in Litres.	$a_{25°}$.	$a_{35°}$.	$K_{25°} \times 10^6$.	$K_{35°} \times 10^6$.	Heat Evolved.
4	·00207	·00164	1·07	·669	8590
8	·00305	·00238	1·16	·705	9120
16	·00430	·00331	1·15	·683	9590
32	·00606	·00468	1·14	·684	9440
64	·00841	·00647	1·11	·650	9740
128	·0118	·00913	1·105	·646	9740
256	·0173	·0140	1·19	·777	7780
384	·0207	·0168	1·14	·748	7690
1024	·0309 ?	·0261	·96 ?	·683	6270 ?

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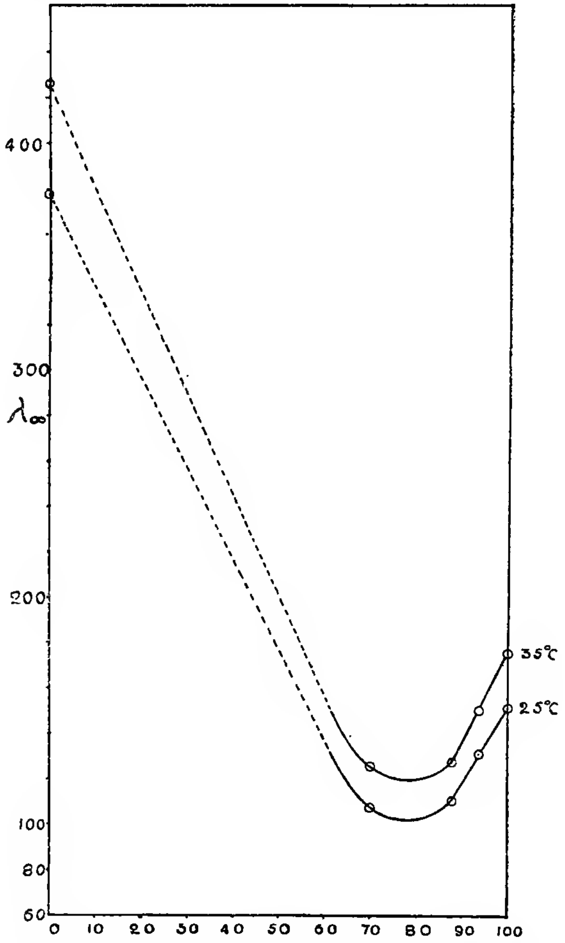
[1] *Cf.* Lewis and Roshdestwensky, *J. Chem. Soc.*, **99**, 2138 (1911).

Neglecting the value for V = 1024, we have the mean heat evolved in ionisation = 8960 cals. per mole.

For picric acid in pure acetone as solvent the results are in good agreement with Ostwald's Dilution Law. The mean values of the dissociation constants are—

Equivalent conductivity at infinite dilution plotted against concentration of acetone in solvent for picric acid at 25° and 35° C.



Weight per cent. acetone in the acetone-water mixture.

FIG. 3.

$$1{\cdot}13 \times 10^{-6} \text{ at } 25^\circ$$
$$0{\cdot}69 \times 10^{-6} \text{ at } 35^\circ.$$

EFFECT OF THE COMPOSITION OF THE SOLVENT ON THE LIMITING EQUIVALENT CONDUCTIVITY, IONISATION CONSTANT, AND HEAT OF IONISATION OF PICRIC ACID, IN MIXTURES OF WATER AND ACETONE.

Per Cent. Acetone (Grams of Acetone in 100 Grams Mixture).	λ_∞ 25°.	λ_∞ 35°.	At Great Dilution.		Average Heat Evolved.
			$K_{25°}$.	$K_{35°}$.	
0	376·1	428·2	·155	·110	4570
70·52	107	125	·072	·069	1700
87·76	110	126·2	·008	·006	5330
93·80	128·5	148	·0017	·0010	8680
100	150 (E)	173 (E)	$1·13 \times 10^{-6}$	$·69 \times 10^{-6}$	8960

(E) extrapolated from the other λ_∞ values.

The minimum in equivalent conductivity at infinite dilution is to be referred to a minimum in the fluidity of the solvent.[1] Assuming that the minimum fluidity on the part of the mixed solvent indicates maximum union of the acetone and water molecules, it is conceivable that, under these circumstances, solvation of the ions would be a minimum. This may explain the fact that under the above conditions the observed heat evolved is likewise a minimum since it is reasonable to assume that formation of a solvate is accompanied by an evolution of heat. This, however, on the simplest basis would lead us to expect that the rate of union of the ions would be specially favoured at this point so that the ionisation constant in respect of this effect should also be a minimum. The fact that it is not so may perhaps be referred to the dielectric properties, *i.e.*, the dissociating power of the above mixture, which is greater than that of mixtures containing greater amounts of acetone,[2] and consequently the rate of ionisation of the (unionised) molecules of picric acid is greater in 70 per cent. acetone water than it is in solutions richer in acetone.

PARANITROBENZOIC ACID.

Paranitrobenzoic Acid in Water.—The acid used was recrystallised twice from acetone, and dried at 120° C. The values given below in the case of water alone as solvent agree well with those of Wrightman and Jones,[3] from whose data the values of λ_∞ are taken, after allowing for the fact that these authors express their results in Siemens units.

Values corrected for specific conductivity of water, namely :—

$1·0 \times 10^{-6}$ mhos at 25°, $1·2 \times 10^{-6}$ mhos at 35°.

Dilution in Litres.	$\lambda_{25°}$.	$\lambda_{35°}$.	$\alpha_{25°}$.	$\alpha_{35°}$.	25° K × 10⁴	35° K × 10⁴.	Heat Evolved.
512	137·0	158·1	·368	·372	4·19	4·30	Zero within the limits of experimental error.
1024	174·8	200·0	·470	·4705	4·07	4·08	
2048	220·0	251 8	·591	·592	4·18	4·20	
∞	372	425					

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[1] *Cf.* Jones and Bingham, *Amer. Chem. J.*, 34, 540 (1905).
[2] *Cf.* Drude, *Zeit. phys. Chem.*, 23, 288, 1897.
[3] *Amer. Chem. J.*, 46, 89 (1911).

PARANITROBENZOIC ACID IN 44·35 PER CENT. AQUEOUS ACETONE.

Values corrected for specific conductivity of solvent, namely :—

1·5 × 10^{-6} mhos at 25°, 1·8 × 10^{-6} mhos at 35°.

Dilution in Litres.	λ_{25°.	λ_{35°.	a_{25°.	a_{35°.	5° K × 10^5	35° K × 10^5.	Heat Evolved.
32	4·47	5·31	·0267	·0267	2·29	2·29	0
64	6·23	7·37	·0372	·0370	2·25	2·22	200
128	8·80	10·40	·0525	·0523	2·27	2·25	100
256	12·29	14·53	·0734	·0730	2·27	2·25	100
512	17·26	20·33	·103	·102	2·31	2·26	300
1024	23·0	27·0	·137	·136	2·12	2·09	200
1280	26·2	30·4	·156	·152	2·25	2·13?	1000?
∞	167·5	199·0					

The values for λ_∞ could not be obtained directly, but were calculated from the observed values of λ_∞ for hydrochloric acid, potassium chloride, and potassium nitrobenzoate, given below.

EQUIVALENT CONDUCTIVITIES IN 44·35 PER CENT. AQUEOUS ACETONE OF—

Dilution in Litres.	Hydrochloric Acid.		Potassium Chloride.		Potassium *p*-Nitrobenzoate.	
	25°	35°	25°	35°	25°	35°
200	174·8	207·4	73·7	90·4	59·36	73·4
400	178·2	212·2	76·4	94·5	61·0	75·4
800	179·6	214·8	77·1	95·2	62·6	77·1
1600	181·4	216·0	77·5	95·4	63·1	77·8
∞	182	217·0	78·0	96·0	63·5	78·0

Assuming Kohlrausch's Law of the Independent Migration of Ions we may write :—

λ_∞ *p*-nitrobenzoic acid − λ_∞ HCl.
= λ_∞ potassium *p*-nitrobenzoate − λ_∞ KCl
whence λ_∞ for *p*-nitrobenzoic acid
= 167·5 at 25°, 199 at 35°.

Referring to the table containing the conductivity data for paranitrobenzoic acid in 44·35 per cent. aqueous acetone, the columns five and six show that Ostwald's Dilution Law is obeyed, as one would expect. The mean values for the ionisation constant are :—

2·25 × 10^{-5} at 25° C.
2·21 × 10^{-5} at 35° C.

The heat of ionisation appears to be about 200 calories evolved, of the same order as the probable maximum error. Thus the heat of ionisation is sensibly the same as in pure water.

SUMMARY.

(1) In passing from pure water as solvent to 93·8 per cent. acetone, the onisation constant of picric acid falls from about 0·2 to ·002, but even in

the latter case the deviation from Ostwald's Dilution Law still manifests itself, and to a similar extent. In anhydrous acetone the ionisation constant for picric acid has fallen to the order 10^{-6}, and Ostwald's Dilution Law is obeyed. The above tends to show that the anomaly of strong electrolytes is to be referred to some property of the system solute plus solvent (in this case picric acid plus water), rather than to high degree of ionisation. (2) The heat of ionisation of picric acid varies largely with the nature of the solvent passing through a minimum at about 70 per cent. acetone. (3) In the case of paranitrobenzoic acid in water, the heat of ionisation is sensibly zero. In 44·35 per cent. acetone the ionisation constant has fallen one-twentieth of its value in pure water, but the heat of ionisation is still sensibly zero.

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University of Liverpool.

THE POTENTIAL OF THE IODINE ELECTRODE, AND THE ACTIVITY OF THE IODIDE ION AT 25° C.

By A. McKeown.

(*A paper read before* The Faraday Society, *Wednesday, June* 22, 1921, Professor Alfred W. Porter, F.R.S., President, *in the Chair.*)

[*Received May* 13*th*, 1921.]

Previous work on the iodine electrode has been carried out by Crotogino,[1] Sammet,[2] Maitland,[3] Laurie,[4] and others.

Crotogino has measured the electro-motive forces of a series of cells of the type:—

Platinum plate + solid iodine	Potassium iodide (c) saturated with iodine	normal calomel electrode .	(A)

for values of c ranging from $\frac{N}{1}$ to $\frac{N}{1024}$. The platinum plate dipped into the solution of potassium iodide saturated with iodine, and diffusion between this solution and the solution of potassium chloride in the calomel half-element was prevented by fixing the potassium chloride solution in the syphon of the half-element by means of gelatin. The temperature to which the measurements applied was 25° C.

An attempt has been made to duplicate these results for various concentrations of potassium iodide, for cells of the type:—

Platinum plate + solid iodine	Pot. iodide (c) sat. with iodine	saturated pot. chloride	normal calomel electrode	(B)

Diffusion between the solutions was not prevented by fixing as in the experiments of Crotogino, since it was found that renewal of the liquid junction between the saturated potassium chloride solution and that of the calomel electrode did not affect the electro-motive force obtained; the liquid junction between the saturated potassium chloride and the potassium iodide-iodine solution was renewed before each reading.

The results obtained differ in almost every case from those given by Crotogino. Both series of determinations for varying values of potassium content are summarised in Table I. following:—

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[1] *Zeit. anorg. Chem.*, 1900, **24**, 225.
[2] *Zeit. physik. Chem.*, 1905, **53**, 641.
[3] *Zeit. Elektrochem.*, 1906, **12**, 263.
[4] *Proc. Roy. Soc.*, Edin. 1908, **28**, 382.

TABLE I.

(1) Dilution of KI.	(2) E.M.F. (Crotogino).	(3) E.M.F. Obtained.
1	0·279 volt	0·2892 volt
2	0·295 „	0·2978 „
4	0·313 „	0·3130 „
10	* 0·339 „	0·3340 „
16	0·351 „	0·3456 „
50	* 0·384 „	0·3708 „
64	0·391 „	0·3764 „
100	* 0·404 „	0·3872 „
256	0·432 „	0·4080 „
1024	0·473 „	0·4400 „

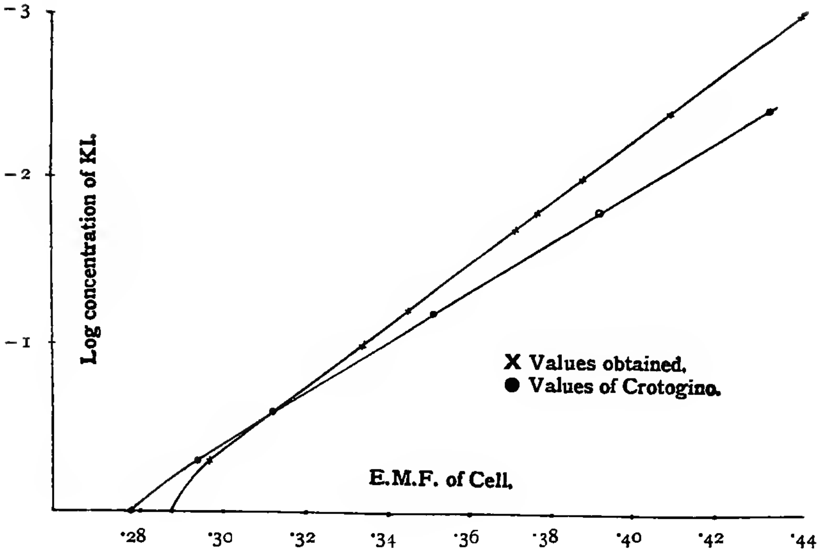

FIG. 1.

The divergence is easily seen from the graphical representation, in which the logarithm of the concentration of potassium iodide (ordinate) is plotted against the electro-motive force of the corresponding cell (abscissa).

It might be thought that the liquid-liquid potentials in the two types of cell are different, and that such a factor would explain away the differences in the results obtained. This was tested experimentally by substituting normal potassium chloride solution for saturated potassium chloride solution in a cell of type (B) for which the concentration of potassium iodide was 0·02N. No change in the E.M.F. of the cell was observed as a result of this substitution. From the theoretical standpoint, we may substantiate this conclusion by an application of the Henderson formula to calculate the liquid-liquid potentials in the two cells:—

$$\text{Pt.} + I_2 \;\Big|\; \frac{N}{50}\ \text{KI sat. with } I_2 \;\Big|\; \text{N calomel} \quad . \quad . \quad (a)$$

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* Interpolated from graph of Crotogino's values.

and

$$\text{Pt.} + I_2 \;\Big|\; \frac{N}{50}\,\text{KI sat. with } I_2 \;\Big|\; \text{sat. KCl} \;\Big|\; \text{N calomel} \quad . \qquad (b)$$

Bray and McKay[1] have derived the following relative values of the mobilities of the ions concerned, from conductivity data of potassium iodide-iodine solutions at 25° C. :—

$$u_{K^{\cdot}} = 74{\cdot}8\,;\; v_{Cl'} = 75{\cdot}6\,;\; v_{I'} = 76{\cdot}5\,;\; v_{I'_3} = 41.$$

Moreover, we may take as a first approximation, that the concentration of I'_3 is equal to that of I' ion for a 0·02N potassium iodide solution saturated with iodine.[2] Hence the concentration of either ion is roughly 0·01N. By substitution of these numerical values in Henderson's formula, we find that the algebraic sum of the liquid-liquid potentials of cell (*a*) is 0·79 milli-volt, tending to make the iodine side more positive. In the case of cell (*b*), this quantity amounts to 0·63 milli-volt, acting in the same sense. The difference is 0·16 milli-volt, which lies within the limit of our experimental error. It is evident, therefore, that the difference in the liquid-junctions used will not explain the discrepancy to be observed in the two series of results given above. The divergence is possibly due to presence of gelatin in the cells used by Crotogino.

It is of interest here to compare the "concentrations" of iodide ion (as determined by electrical conductivity) in the various potassium iodide-iodine solutions used with the activities of the iodide ion obtained from the E.M.F. data. This is done in Table II. below. The values given for the concentration of iodide ion have been obtained from the data of Bray and McKay[3] (*loc. cit.*) on the conductances and composition of solutions of potassium iodide saturated with iodine at 25° C. Thus for 0·01NKI solution saturated with iodine, the total iodine dissolved is $6{\cdot}185 \times 10^{-3}$ gm. mols. per litre. The concentration of free iodine is given by the solubility of iodine in water, *viz.*, $1{\cdot}32 \times 10^{-3}$ gm. mols. per litre. Hence the concentration of KI_3 is $4{\cdot}865 \times 10^{-3}$. The difference between this and the concentration of potassium salt originally present gives the amount of KI present as $5{\cdot}135 \times 10^{-3}$ gm. mols. per litre. The percentage ionisation of the salt being 94·1, the concentration of iodide ion in the solution is $4{\cdot}83 \times 10^{-3}$.

From the E.M.F. data given in column (3) of Table I., the activity of iodide ion in the various solutions may be calculated, on the supposition that the activity of iodide ion is equal to its concentration in the most dilute solution used. The relation between the activity of iodide ion *a* and the E.M.F. of the corresponding cell E, is contained in the equation :—

$$E = E_0 - {\cdot}0591 \log a$$

where E_0 is the normal potential (with respect to activity) of the (saturated) iodine electrode, the normal calomel electrode potential being taken as zero. The concentration of iodide ion in $\frac{N}{1024}$KI solution saturated with iodine is given by Bray and McKay as $\cdot 000509 \pm \cdot 00001$. Substituting $a = \cdot 000509 \pm \cdot 00001$ and $E = \cdot 440$ volt in the above equation, we find

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[1] *Journ. Amer. Chem. Soc.*, 1910, **32**, 914.

[2] Bray and McKay, *loc. cit.*, find that $C_{I'}/C_{I'_3} = 1{\cdot}04$ for this particular solution.

[3] Jones and Hartmann, *Journ. Amer. Chem. Soc.*, 1915, **37**, 241, have corrected the data of Bray and McKay for viscosity, but this correction is small, and is within the limits of error of these data.

E_0 = ·2454 ± ·0004 volt. Using the value E_0 = ·2454 volt in the same equation, the activities of iodide ion in the other solutions are calculated.

TABLE II.

(1) Cooc. of KI.	(2) Conc. of I′.	(3) Activity of I′.	(4) Conc. of I'_3.	(5) Activity of I'_3.
·25	·0980	·0718	·1126	·0630
·10	·0431	·0316	·0444	·0278
·0625	·0277	·0210	·0278	·0185
·02	·00938	·00755	·00904	·00662
·015625	·00744	·00607	·00710	·00532
·01	·00483	·00398	·00458	·00349
·003906	·001956	·001774	·001819	·001556
·000976	·000509	·000509	·000446	·000446

From the table it is seen that the divergence between the concentration and the activity of the iodide ion becomes greater as the concentration increases, the activity being always less than the concentration. The direction of the divergence is the same qualitatively as has been found by Harned to hold for the case of solutions of potassium chloride.[1] Quantitatively, the ratio of concentration to activity of iodide ion in ·25NKI solution saturated with iodine is 1·36 : 1. In a potassium chloride solution of the same strength the results of Harned give the ratio of concentration to activity of the chlorine ion as 1·19 : 1.

Again, in columns (4) and (5) of Table II., the values of the concentration and activity of the tri-iodide ion in the various solutions have been compared. The concentration data are derived from the work of Bray and McKay already quoted. These writers have found that in potassium iodide solutions saturated with iodine the ratio of the concentration of iodide ion to that of tri-iodide ion, which according to the law of mass action should be constant, decreases from 1·14 to 0·99 when the potassium salt increases from 0·001 to 0·1 N. If the activities of the ions be substituted for their concentrations in the mass action equation:—

$$I' + I_2 \rightleftharpoons I'_3$$

the ratio of the activities of iodide ion and tri-iodide ion should remain constant for all values of the potassium salt concentration. Since it is assumed that activity is equal to concentration at great dilution, it follows that the ratio of the activities of the ions at great dilution should have the same value as the ratio of their concentrations at the same dilution, namely 1·14. This value has been used, together with the activity data in column (3) of Table II., to calculate the activities of the tri-iodide ion in the various solutions, given in column (5). Here again the activity of the ion is much less than its concentration in the stronger solutions, the values becoming closer in agreement as the dilution increases. The ratio of the concentration to the activity of the tri-iodide ion in the ·25 NKI solution saturated with iodine is 1·79 : 1.

Hence in potassium iodide solutions saturated with iodine, the activities of the iodide ion and the tri-iodide ion increase less rapidly than their concentrations, the divergence being more marked for the case of the tri-iodide ion.

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[1] *Journ. Amer. Chem. Soc.*, 1916, 38, 1989.

Reverting to the iodine electrode, it has been found above that the normal potential E_0 is equal to ·2454 ± ·0004 volt at 25° C., the potential of the normal calomel half-element being taken as zero, and this value has been used to find the activities of iodide ion in various KI-I_2 solutions. The usually accepted E_0, *viz.*, ·256 volt, has been derived by Sammet[1] from the results of Crotogino already quoted, Jakowkin's data being used to obtain the concentration of iodide ion in the various solutions. Not only do these concentration data differ from those of Bray and McKay, but the value of the normal potential $E_0 = \cdot 256$ volt is calculated from the E.M.F. and concentration of the strongest solutions used, in which, by analogy with recent results for other salts, it is most probable that there is great divergence between activity and concentration. The value $E_0 = \cdot 2454$ volt, however, has been derived from data of very dilute solutions, in which activity and concentration may be assumed to be equal. Of course, this value of E_0 refers only to the saturated iodine electrode. If the activity of free iodine in solution be also variable, the formula applying is

$$E = E'_0 + \frac{\cdot 0591}{2} \log \frac{(\text{activity of } I_2)}{(\text{activity of } I')^2}$$

and E'_0 has the value ·2454 + ·0851, that is ·3305 volt.

Summary.

Electro-motive force measurements have been made for cells of the type :—

Pt + I_2 | KI solution sat. with I_2 | sat. KCl | N calomel electrode
the concentration of potassium iodide being varied between wide limits.

From the results the activities of the iodide ion and the tri-iodide ion in the various solutions have been calculated. It is found that the activities of both ions increase less rapidly than their concentrations.

The potential of the normal (saturated) iodine electrode has been deduced in terms of the activity of the iodide ion. The value found is + ·2454 volt, the normal calomel electrode being taken as zero.

This work, which is the preliminary of a wider investigation, was carried out at the suggestion of Professor W. C. M. Lewis, to whom I here wish to express my thanks.

Muspratt Laboratory of Physical Chemistry,
University of Liverpool.

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[1] *Zeit. Physik. Chem.*, 1905, **53**, 674.

THE RECRYSTALLISATION OF THE COPPER-ZINC ALPHA SOLID SOLUTION.

BY MAURICE COOK, M.SC., KING'S COLLEGE, CAMBRIDGE.

(*A Paper read before* THE FARADAY SOCIETY, *Wednesday, June* 22, 1921, PROFESSOR ALFRED W. PORTER, F.R.S., PRESIDENT, *in the Chair.*)

The change of structure and the consequent changes in mechanical properties resulting from the annealing of some of the chief industrial alloys of copper, particularly the brasses and bronzes, have engaged the attention of many investigators. The investigations of Charpy,[1] Bengough and Hudson,[2] Mathewson and Phillips,[3] Smith,[4] Bassett and Davis,[5] and Phillips and Gerner,[6] all dealt with the annealing, recrystallisation, grain, growth, etc., of brass which had been previously worked.

The present author has studied the recrystallisation or homogenisation of an unworked alpha brass containing 30 per cent. of zinc and 70 per cent. of copper. When such an alloy as this is cast in a chill mould the first solid particles which separate out are richer in copper than the melt. As cooling proceeds, further deposition of solid particles takes place on those previously deposited, but they are not so rich in copper, and this separation of a solid from a melt gradually becoming poorer in copper, continues until the whole alloy is frozen, giving rise to the well-known cored or dendritic structure. It is obvious that the coring results from cooling which is sufficiently rapid to prevent the attainment of equilibrium between the deposited solid and the melt, and also that if the cooling was slow enough to allow interdiffusion to take place the solidified metal would then consist of perfectly homogeneous crystals and not of dendrites varying in composition from the cores outwards. From this it follows that the degree of coring in an alloy such as the one under consideration is very largely governed by the rate at which it solidified. Attempts have been made to find out at what temperatures, with varying periods of annealing, the cored or heterogeneous crystals become homogenised.

The materials used in the preparation of the alloy were kathode copper and Mond's electrolytic zinc. The brass was made in the ordinary way, and a number of small ingots weighing about 150 grammes each were cast in half-inch open iron moulds. It was imperative that each specimen be cast as a separate unit, for any sample cut off from a larger piece of brass could not be considered as an unworked specimen since it is a well-known fact that brasses which have been merely gripped in a vice and sawn exhibit unmistakable signs of this work—*e.g.* prolific crystal twinning—when examined microscopically after annealing. In order that the original structure of the ingots should in all cases be as near alike as possible the conditions of casting were kept the same throughout. The metal was cast at a temperature as little above its freezing-point as convenient to pour, and a like amount of metal poured into each mould. In this manner some sixty small cylindrical ingots were prepared with presumably the maximum chilling effect, for the degree of chilling is greater the lower the casting temperature. Cooled under these conditions the alloy is made up entirely of heterogeneous cored crystals.

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[1] G. Charpy, " Contribution à l'étude des alliages," Paris, 1901.

[2] G. D. Bengough and O. F. Hudson, *Journ. Inst. Met.*, II, 1910.

[3] C. H. Mathewson and A. Phillips, *Trans. Amer. Inst. Min. Eng.*, 1916, Vol. LIV.

[4] F. G. Smith, *Bull. Amer. Inst. Min. and Met. Eng.*, 1919, No. 152, 1361.

[5] W. H. Bassett and C. H. Davis, *Trans. Amer. Inst. Min. and Met. Eng.*, 1919, Vol. LX, 428.

[6] A. Phillips and G. C. Gerner, *Chem. and Met. Eng.*, 1919, XX, 622

The cast unworked ingots were annealed in a small electrically heated muffle furnace for different periods of time at different temperatures. In each case some fifteen minutes were allowed for the specimen to attain the temperature of the furnace. It was soon noticed that, for the comparatively short annealing periods adopted in the present work, at moderately low temperatures, *e.g.* 400° to 500° C., no perceptible change in the original structure occurred. The cored structure is, at low temperatures, a very stable one and shows not the least tendency to become homogenised. When the annealing temperature reached 600° C. the change of structure became very marked with different periods of annealing, whilst any specimen annealed at 650° C. for more than one hour became completely homogenised, there being no trace of coring visible.

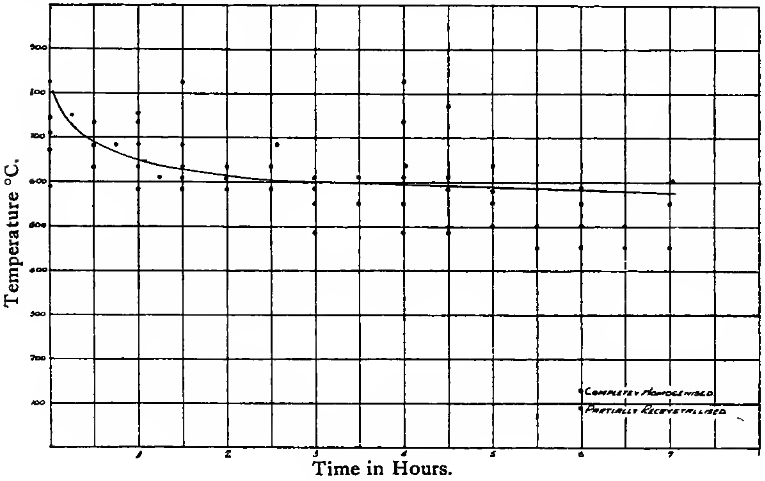

FIG. 1.

Having ascertained that annealing for periods not exceeding seven hours at temperatures below about 550° C. could not entirely homogenise the alloy the following plan was adopted. A number of the ingots were introduced into the furnace at 550° and one removed every half-hour. When the whole 550° series had been annealed they were polished and examined. The next set of samples was annealed at about 600° C., the next at about 650° C. and so forth. In Fig. 1 is shown a curve drawn from information derived from these annealing experiments. Specimens completely homogenised are represented by black dots, those partially homogenised by small circles. Above the curve is the region of complete recrystallisation or homogenisation, that is to say, the structure of any specimen annealed in the zone lying above the curve consists entirely of homogeneous polygonal grains. Immediately below the line is a region of partial recrystallisation. Here the annealing has been such as to allow a restricted interdiffusion to take place, and the structures vary from the markedly cored such as found in an original unannealed sample to the almost homogeneous polygonal grains. Below this region the annealing has not altered the original structure, but no attempt has been made to shed the limits of the zones of partial and non-recrystallisation, for there is no doubt but what the transition is certainly not sharp and distinct and hence incapable of exact determination. Nevertheless, it seems from a careful examination of the structures of a large number of specimens that the region of partial recrystallisation is not great in extent, for the original cast structure does not appear to change in any way until the annealing temperature is within 200° or 300° of the curve bounding the region of complete homogenisation. In order to determine this curve with still greater accuracy more annealings were made at temperatures between 600° and 650°, 650° and 700° and so forth with time intervals of fifteen minutes. No attempt has been made to classify the degree or extent to which coring remains in the partially homogenised specimens and to draw the corresponding curves, for such classification is purely arbitrary and unsatisfactory, though it has been attempted in the case of certain bronzes by Mathewson and Davidson.[1]

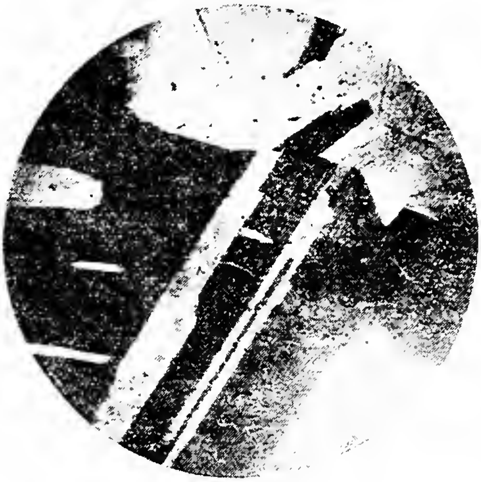

FIG. 2.

Regarding the mechanism of the process of homogenisation little need be said, for it is merely, in the first place, a case of diffusion in the solid state facilitated by increase of temperature. It would seem that one dendrite can give rise to more than one polygonal grain, and also that several dendrites may ultimately be merged into only one grain.

Fig. 2, which shows the structure of a specimen annealed at 825° for four hours, is reproduced as illustrating the fact that twin crystals can be produced in a casting upon which no work whatsoever has been done prior to the annealing.

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[1] C. H. Mathewson and P. Davidson, *Inter. Zeit. Met.*, VIII, 1916, 181.

NOTE ON THE HYDROLYSIS OF A SALT FORMED FROM A WEAK ACID AND A WEAK BASE.

By R. O. Griffith.

(*A Contribution to the* Transactions *of* The Faraday Society. *Received 28th June*, 1921.)

The object of this short paper is to point out a feature of the hydrolysis of salts formed from a weak acid and a weak base which is not explicitly stated and is perhaps overlooked in the method of treatment usually adopted in textbooks of physical chemistry.

This treatment is somewhat as follows.[1]

Consider one gram-molecule of the salt dissolved in v litres of water, and indicate the degree of hydrolysis, by x, that is the quantity of free acid and free base formed by the water per mole of salt. Then assuming (1) that the salt is completely dissociated into its ions, (2) that the weak acid and the weak base are practically undissociated, the following equations hold:—

$$\frac{[\mathrm{H}^{\cdot}] \cdot \frac{1-x}{v}}{\frac{x}{v}} = k_a, \text{ the dissociation constant of the weak acid;}$$

$$\frac{[\mathrm{OH}'] \cdot \frac{1-x}{v}}{\frac{x}{v}} = k_b, \text{ the dissociation constant of the weak base;}$$

$$[\mathrm{H}^{\cdot}]\,[\mathrm{OH}'] = \mathrm{K}_w, \text{ the ionic product of water,}$$

whence

$$\frac{k_a k_b}{\mathrm{K}_w} = \frac{(1-x)^2}{x^2}$$

that is, the fraction of the salt hydrolysed does not depend on the dilution. It also follows, as pointed out by Tizard,[2] that the hydrogen ion concentration is also independent of the dilution, since

$$[\mathrm{H}^{\cdot}] = k_a \frac{x}{1-x} = k_a \sqrt{\frac{\mathrm{K}_w}{k_a k_b}} = \text{a constant.}$$

These conclusions, while true for solutions of ordinary concentration, require slight modification in extremely dilute solutions—owing to assumption (2);

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[1] See for example, Abegg, "Electrolytic Dissociation Theory," trans. by Von Ende, p. 89.

[2] *Trans. Chem. Soc.*, 97, 2494 (1910).

no longer being true—and the treatment of such a case indicates that the degree of hydrolysis of the salt is made up of two such terms (one for each ion) which are identical in stronger solutions. Thus let us consider one mol of the salt BA, aniline acetate, giving rise to $B^{\cdot}$ ("anilinium" ions) and A' (acetate ions), dissolved in v litres of water, and as before assume that the salt is completely dissociated. The dissociation constants k_a and k^b of the weak acid HA (acetic) and base BOH (aniline) we may take as $1{\cdot}8 \times 10^{-5}$, and $4{\cdot}2 \times 10^{-10}$ respectively, and the ionic product of water as $1{\cdot}1 \times 10^{-14}$.

We then obtain the six equations :—

$$\frac{[H^{\cdot}]\,[A']}{[HA]} = k_a = 1{\cdot}8 \times 10^{-5} \tag{1}$$

$$\frac{[B^{\cdot}]\,[OH']}{[BOH]} = k_b = 4{\cdot}2 \times 10^{-10} \tag{2}$$

$$[H^{\cdot}]\,[OH'] = K_w = 1{\cdot}1 \times 10^{-14} \tag{3}$$

$$[A'] + [HA] = \frac{1}{v} \tag{4}$$

$$[B^{\cdot}] + [BOH] = \frac{1}{v} \tag{5}$$

$$[H^{\cdot}] + [B^{\cdot}] = [A'] + [OH'] \tag{6}$$

equation (6) being the condition for electrical neutrality. From these equations, fixing a value for v, the values for $[H^{\cdot}]$, $[OH']$, $[A']$, $[B^{\cdot}]$, [BOH] and [HA] may be calculated at the required dilution.

Thus, taking first $v = 5000$, or a salt concentration of 2×10^{-4}, we find for this dilution

$$\begin{aligned} [H^{\cdot}] &= 1{\cdot}79 \times 10^{-5} & [OH'] &= 6{\cdot}144 \times 10^{-10} \\ [A'] &= 1{\cdot}003 \times 10^{-4} & [B^{\cdot}] &= 0{\cdot}812 \times 10^{-4} \\ [HA] &= 0{\cdot}997 \times 10^{-4} & [BOH] &= 1{\cdot}188 \times 10^{-4} \end{aligned}$$

It will be observed that, at this concentration of salt, [HA] is not equal to [BOH], *i.e.* the degree of hydrolysis differs for each ion. If we take as the degree of hydrolysis of an ion the fraction converted into undissociated acid or base, then the fraction of A' ions hydrolysed is

$$\frac{0{\cdot}997 \times 10^{-4}}{2{\cdot}00 \times 10^{-4}} = 0{\cdot}4985,$$

since $2{\cdot}00 \times 10^{-4}$ would be the concentration of A' ions if no hydrolysis had occurred, while, in a similar manner, the degree of hydrolysis of the $B^{\cdot}$ ions is

$$\frac{1{\cdot}188 \times 10^{-4}}{2{\cdot}00 \times 10^{-4}} = 0{\cdot}594.$$

This behaviour may be contrasted with that of a stronger solution, taking as example $v = 50$, or concentration of salt $= 2 \times 10^{-2}$.

From equations (1) to (6) we now find

$$\begin{aligned} [H^{\cdot}] &= 2{\cdot}17 \times 10^{-5} & [OH'] &= 5{\cdot}06 \times 10^{-10} \\ [A'] &= 0{\cdot}907 \times 10^{-2} & [B^{\cdot}] &= 0{\cdot}907 \times 10^{-2} \\ [HA] &= 1{\cdot}093 \times 10^{-2} & [BOH] &= 1{\cdot}093 \times 10^{-2} \end{aligned}$$

Here [HA] = [BOH], and the fraction of A' hydrolysed = fraction of B hydrolysed $= \frac{1{\cdot}093 \times 10^{-2}}{2{\cdot}00 \times 10^{-2}} = 0{\cdot}5465$, agreeing with the value of x obtained from the usual formula

$$\frac{x^2}{(1 - x)^2} = \frac{K_w}{k_a k_b}$$

from which $x = 0{\cdot}5468$.

It thus appears that for such salts it is necessary to state more exactly what is meant by the term "degree of hydrolysis" when the solution is very dilute, in the case of aniline acetate, for example, when the dilution is greater than 1000.

One other result of the calculation may also be noted, *viz.* that the hydrogen ion concentration of a solution of aniline acetate, while practically constant down to $v = 500$, should not be independent of the concentration between $v = 500$ and $v = 5000$, but should fall with increasing dilution.

It is found that when $v = 50$ $[H^{\cdot}] = 2{\cdot}17 \times 10^{-5}$
$v = 500$ $[H^{\cdot}] = 2{\cdot}13 \times 10^{-5}$
$v = 5000$ $[H^{\cdot}] = 1{\cdot}79 \times 10^{-5}$

This conclusion has not been experimentally verified, Tizard (*loc. cit.*), who found a constant hydrogen ion concentration of $2{\cdot}29 \times 10^{-5}$ for solutions of strength between $\frac{N}{20}$ and $\frac{N}{500}$, not extending his measurements beyond the latter limit.

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REVIEWS OF BOOKS.

A Text-Book of Inorganic Chemistry for University Students.

By J. R. PARTINGTON, M.B.E., D.Sc. (London, 1921: Macmillan & Co. Pp. xii + 1062. Price 25s. net.)

Certain Universities still permit students to enter upon a course of chemistry without insisting upon an accompanying course in physics. Consequently the author of a text-book on "Inorganic Chemistry" has to burden his work with an exposition of some of the fundamental principles of physics. One looks forward to the day when this will no longer be necessary. In the present work the purely physical portion is remarkably lucid considering the high degree of compression achieved, but the sound knowledge of physics required to-day for the study of chemistry cannot be obtained from such a summary, excellent though it be. The important applications of physics to chemistry are dealt with, in most cases amply, and the historical treatment of many theories is a great aid to their understanding. The molecule is dealt with in a convincing way, but one regrets that the space allotted to the structure of the atom is so small, in view of the recent work of Aston on isotopes, and of Rutherford on the disintegration of nuclei. Indeed Aston's work is a powerful reason why atomic weights should be referred to the standard O = 16 and not to H = 1, as is done. Apparently the electron theory of valency finds no place. The application of the phase rule to various problems might well have been extended considering how great a help it is to the understanding and memory.

The discussion of the atomic theory is excellent, and students will derive great benefit from the clear treatment of the composition of various compound gases and the accurate descriptions of many examples of equivalent weight determination. The accounts of the method of limiting densities and of the theory of indicators are also welcome features.

The elements are treated systematically according to the periodic system and compounds whose existence is doubtful or whose interest is small are omitted. Manufacturing processes are dealt with in a practical manner, and it is satisfactory to note diagrams of modern plant such as Gaillard towers and vacuum pans. Usually, too, the chief mode of preparation of any particular product is particularised and also its technical uses.

The type employed is good but often the diagrams are poorly drawn. Needless to say, throughout the book the matter is thoroughly up to date. Although inorganic text-books are galore, there should be room for a work like this, both on account of such valuable features as are mentioned above and of its readable, lively style. But its price is a great handicap.

Dictionary of Applied Chemistry. Edited by SIR EDWARD THORPE, C.B., LL.D., F.R.S. Assisted by Eminent Contributors. Revised and Enlarged Edition. Vol. II.: Calculi—Explosion. (London, 1921: Longmans, Green & Co. Pp. 717. Price 60s. net.)

The appearance of the second volume of the new edition of Thorpe's Dictionary has followed closely on the publication of the first volume. Of the more important articles mention may be made of Carbohydrates, Carbon, Chlorine, Cinchona Alkaloids, Copper, Cyanides, Disinfectants, Distillation, Dyeing and Explosion, Gaseous. The volume deals, too, with quite a number of themes which have formed the subject of general discussions at meetings of the Faraday Society. Colloids, Clay, and Corrosion may be instanced in this connection.

It is to be regretted that the important subject of Colloids should have been compressed into four pages in view of the innumerable industrial processes in which they are involved. and any attempt at justifying such a short article on the grounds of the necessity of compelling contributors to present their facts in the shortest possible space is easily upset by a consideration of the article on Chlorine. In this article one reads in connection with the electrolytic production of the gas, "Lepsius . . . says, with German pride . . . and while he pities the fate of poor Leblanc, yet he concludes with characteristic German military imagination and arrogance, . . . that the bitter international struggle between the old process . . . and its two younger rivals, is now finished . . . because there appeared a German rival." Further on is a paragraph devoted to the use of chlorine as a poison gas. It commences "The poisonous properties of chlorine were first used in warfare by the Germans. . . . A German deserter . . . gave warning of the first attempt to use poison gas in modern warfare. No one believed him . . . the German war of frightfulness was made to include chemical frightfulness . . ." and so on. A Dictionary of Applied Chemistry is not the place for the expression of political opinions and the space could have been filled to much better purpose.

For the new edition of the Dictionary many of the articles have undoubtedly been revised and that, too, very thoroughly. However, this is not always the case, and the usefulness of the work would have been enhanced if, for example, the Editor had been able to arrange for that eminent agriculturist, Sir A. D. Hall, to rewrite his valuable articles on "Cereals" and "Crops" in the light of the facts elicited by recent researches.

In connection with the remarks made when the first volume was reviewed as to the need for an index to each volume, it may be pointed out that the reviewer has been able to find a reference to calcium thiocyanate neither in the article on "Calcium" nor in the article on "Cyanides". Attention has been called to this point in view of a recent important paper on the solvent action of calcium thiocyanate solutions on cellulose.

It was previously pointed out, also, that no mention of the production of alcohol from coke oven gas could be found in the article on "Alcohol". However the subject is discussed in the present volume under "Coke Manufacture". One finds it a little difficult to understand why it should be necessary to look for "Animal Charcoal" under the heading of "Decolorising Carbons". The reader is often called upon to exercise no little ingenuity and patience before he has exhausted all the possible headings under which some needed information may be hidden away.

Finally it may be mentioned that, as is usual with works of this class, illustrations and diagrams are included wherever necessary, and that though errors are to be found, they are not very numerous.

Notes on Chemical Research. By W. P. DREAPER, O.B.E., F.I.C. Second Edition. (London, 1920: J. & A. Churchill. Pp. 195. Price 7s. 6d. net.)

Since the time of Francis Bacon some have thought that the acquisition of all natural knowledge can be made possible by the mere organisation of research. It is true that this view has not been held by the great masters of science, who have realised that insight, imagination and inspiration are necessary for discovery in science no less than for creation in art. But the heresy persists in certain quarters and it will be found to constitute no negligible a factor in the policy of many a government department and research association. This particular heresy has a counter-heresy, prevalent in the popular press and among the general public; namely, that scientific discovery and invention come about through an "idea" coming into one's head. If any student of chemistry harbours any such heresy as this he will be well advised to read these notes of Mr. Dreaper, and if he has ideas as well as a sound knowledge of the fundamental facts and principles of his science, his work may really be guided into creative or productive channels.

The present edition is a considerable enlargement of the first edition and it is divided into two main sections, the first dealing with "Scientific Fact and Method," and the second with "Practical Research". The argument throughout is on the whole sound and the advice invaluable, although we cannot agree with the dictum that to ensure knowledge having ultimate value one should work in practical directions. Certainly the author does not appear to intend this advice to be taken quite literally, but as it stands it is misleading, if not mischievous. The earliest researches in radioactivity had no special "end" in view at all and were in a sense almost accidental; they certainly were not based in "practical ideas". The same applies, to an even greater degree, to much astronomical research.

The author rightly deprecates the complete distinction often made between so-called "pure" and "applied" research, but we doubt whether his suggestion to rename these "static" and "dynamic" respectively will be generally acceptable. Much industrial *ad hoc* research is decidedly static rather than dynamic, while to call such work as Rutherford's on the structure of the atomic nucleus "static" would be a decided misnomer

We think that Roger Bacon, rather than the founders of the Royal Society, deserves to be recorded as the father of English science, although at the time the world was not ripe for his work.

We hope that in future editions such names as "Grotthaus," "J. J. Thompson," and "Häber" will be spelt accurately. These inaccuracies are not trivial in a book of this character.

A French-English Dictionary for Chemists. By AUSTIN M. PATTERSON, PH.D. (New York, 1921: John Wiley & Sons; London: Chapman & Hall. Pp. 384. Price 18s. net.)

This is a companion to the author's German-English Dictionary published some years ago, and it will be equally welcomed by all who have to read foreign technical literature. There can obviously be no finality in a work of this kind, but so far as we have been able to test the dictionary it has not failed. The author invites readers to draw his attention to any errors or omissions they may detect. The book has some particularly commendable features; it is neat and handy in form, is very clearly printed, and the author has been generous in giving the several variations in meaning where the French word is more comprehensive than any one English equivalent.

A Text-Book of Physics. By the late W. WATSON, C.M.G., A.R.C.S., D.Sc., F.R.S. Seventh Edition. Revised by HERBERT MOSS, M.Sc., A.R.C.S., D.I.C. (London, 1920: Longmans, Green & Co. Pp. 976. Price 21s. net.)

This is the second edition of the late Col. Watson's text-book produced under the direction of Mr. Moss, and teachers of physics will be grateful to him for making it possible for them still to use so well-tried a guide to physics. The merits of the book are too well known to have attention called to them now. The bigger question arises as to whether it is wise to continue to issue a book of this kind again and again without more drastic overhauling and re-writing than are implied in the conventional phrase "revised and brought up-to-date". We question neither the wisdom of bringing up the student on the foundations of classical physics, nor the excellence and comprehensiveness of Watson's "Physics" in carrying out that aim, but to tell the truth, as it stands, the book is written too exclusively from the standpoint of nineteenth century physics and from its pages alone, few students will realise the developments that have more or less revolutionised physics and many physical conceptions during the past fifteen or twenty years. There is no mention of the Michelson-Morley experiment and what it implies, no mention of quanta, no reference to the Kaufmann experiment and the idea of "electro-magnetic mass". A statement on page 140 suggests that modern views on atomic constitution are a kind of interesting alternative to the Helmholtz-Kelvin vortex atom. Certainly sections have been added on radio-activity, X-ray analysis, electrons and so forth, but there is little that will make the student realise how all this recent work is modifying some of the fundamental conceptions of the physicist. A simple mathematical proof of the Zeeman effect is an omission that calls for notice. There is no reference to Brownian motion.

When all is said this remains an admirable and an extremely useful text-book. It is pre-eminently *safe*. The teacher whose students use it will, however, have to prepare their minds to understand that physics is not quite the complete, self-sufficing fabric that the classical treatment would appear to suggest, but that the science at present is moving forward with unprecedented speed, and almost destructive energy, and it may be passing through a phase comparable in importance with that of the great days when Galileo and Newton were laying its foundations.

La Loi de Newton est La Loi Unique. By MAX FRANCK. (Paris, 1921: Gauthier-Villars et Cie. Pp. 158. Price 12 fr. 50 c.)

It will be best in this case to state the author's thesis in his own words. Here it is:—

"L'Espace n'est composé que de deux éléments: l'un, auquel nous donnons le nom de *positif*, est l'élément agissant, il est la Force, il est immobile et indivisible. S'il était seul à occuper l'espace, aucune manifestation ne serait possible; c'est pourquoi la présence d'un élément passif est indispensable; c'est celui que nous désignerons sous le nom de *négatif* parce qu' il est tout simplement la négation du premier et que sa seule propriété est d'être sans force, d'être inerte et de subir l'action du premier *sans réagir*."

This hypothesis—that matter is a hole in a field of force—is applied to most of the known branches of physics and to a demonstration of the immortality of the soul. It would doubtless have interested Descartes; it may even now be practical metaphysics, but most certainly it is not experimental physics!

Physique Élémentaire et Théories Modernes. By J. Villey. Maître de Conférences à la Faculté des Sciences de Caen. (Paris, 1921: Gauthier-Villars et Cie. Pp. x + 197 with twenty-three figures. Price 15 fr.)

This book is of a type seldom met with in English publications. It presents in a simple way a course of physics of approximately intermediate standard from the view point of the kinetic theory of matter. It is popular in so far that mathematics is reduced to a minimum and the results of various theorems are given without proof; but on the other hand it takes the reader through an ordered course—mechanics, hydrostatics, heat, elasticity and sound—without aiming, in any way, at the simplification of the language of the ordinary text-book. It would make most admirable reading for a science student desirous of polishing up his scientific French during his first long vacation. The book forms only the first part of the whole volume, the second part, dealing with magnetism, electricity and optics is already written and is presumably now passing through the press.

Ions, Electrons, and Ionizing Radiations. By J. A. Crowther, Sc.D. Second Edition. (London, 1921: Edward Arnold. Pp. 276. Price 12s. 6d. net.)

The subject of the properties of electrons and their numerous modes of manifestation and the energy changes associated therewith, is becoming so vast a branch of physics that the student who has not specialised in it is likely to become bewildered in his attempt to understand and co-ordinate phenomena covering so diverse a field. A book of this type was therefore urgently needed, and Mr. Crowther deserves our sincere thanks for having produced it. It is not of course intended to replace the works of Thomson, Rutherford, Richardson, the Braggs, and others of a like calibre, but it is admirably fitted to serve as an introduction to the bigger works, and indeed we know of no other text-book that can be so safely recommended for that purpose to the properly equipped student. The last qualification is used advisedly, because although no very advanced mathematics is employed, a sound knowledge of the fundamental electrical laws is assumed. Given this, any student should master this book with ease, for the reasoning is clear and concise and the happy combination of experimental and mathematical treatment makes the author's presentation most attractive.

The subjects covered include gaseous ions and ionisation, the phenomena of vacuum discharges with their associated radiations, thermionic emission and photoelectricity, X-rays, radioactivity and α, β, γ rays, and finally the electron theory of matter—truly a formidable list to crowd into less than 300 pages. But the author succeeds because he has exercised his selection of material with the utmost care. Everything that is fundamental is touched upon, and the experimental landmarks are emphasised in such a way that they are bound to impress themselves on the careful reader.

The Physical Properties of Colloidal Solutions. By E. F. Burton. Second Edition. Pp. viii + 221. (London, 1921: Longmans, Green & Co. Price 12s. 6d. net.)

This work, the first edition of which appeared in 1914, should be entitled "The Physical Properties of Suspensoid Solutions," as the emulsoids receive passing reference only. As the book is written by a physicist and forms one of a series of monographs on physics, the preference for that branch of the subject which has to some extent been amenable to mathematical or at least quantitative treatment is intelligible, but the intending purchaser ought to have some intimation of this limitation.

Within the scope chosen the treatment is very full and lucid, and, with a few exceptions to be noted, recent work has been included. Particularly admirable are the chapters on the Brownian movement (which occupies a fifth of the whole book) and that on the movement of particles in an electric field, the latter a portion of the subject to which the author has made important contributions. The chapter on electrolyte coagulation very fairly summarises the present position of this much investigated problem, and the author makes some novel and very interesting suggestions regarding the great difference between uni- and tervalent ions, which deserve experimental testing. The theory of the microscope and the ultra-microscope is also treated with unusual fulness. A good summary is given of V. Weimarn's work and—as far as we are aware, for the first time—his failure to consider the electric charge as a factor in sol formation is very fairly pointed out.

Detailed criticism is called for on a few points only. The "envelopment" theory of protective action always involved considerable difficulties, greatly increased by W. Ostwald's work on "Kongo Rubin" (1919), which can be "protected" *after* coagulation. Freundlich's assumption that different ions are adsorbed to the same extent is hardly tenable in view of Ostwald's criticisms and even his own material. That surface tension plays any important part in the aggregation during coagulation is a position which appears to be gradually abandoned (*cf.* especially R. Zsigmondy, *Kolloidchemie*, III. Auflage) and V. Smoluchowski disregards it in his theory of coagulation velocity. In the section on the effect of radiations the very important investigation on cerium hydroxide sol by Pauli and Fernau (1917) should have been mentioned.

The book will be read with interest and profit by all students whose interests go beyond the merely qualitative or utilitarian aspects of the subject.

The Fixation of Atmospheric Nitrogen. By Joseph Knox, D.Sc. Second Edition. (London, 1921: Gurney & Jackson. Pp. 124. 4s.)

This monograph, which first appeared in 1914, is probably well known to the majority of persons interested in nitrogen fixation. The work under review—the second edition—is written on the same general lines as before, and contains a few alterations and some additions, the most important of which concern the oxidation of ammonia.

The chief impression gained from a perusal of this edition is that the subject matter has not been sufficiently brought up to date. According to the author, "comparatively little work of importance on the theoretical side of nitrogen fixation has appeared since 1914," and one finds that, of the 169 references given at the end of the book, only seventeen are dated later than the year named. Recent work on such important subjects as the absorption of oxides of nitrogen and the ammonia equilibrium is omitted. But Dr. Knox states that, "on the other hand, the development of fixation processes on the technical side received an enormous impulse under the stress of war conditions". Nevertheless, there is no addition to the original account of the Birkeland-Eyde furnace and no mention is made of the new and modified plant erected at Rjukan. A similar remark applies to the description of the cyanamide process, and an account of the plant used during the war at Oppau and at Merseburg using the Haber method of ammonia synthesis might have been introduced. On the other hand, eight valuable pages are devoted to the Serpek process (which is no longer worked), whereas the apparently successful Claude process, which is now exciting much interest, is dismissed with a few lines.

The author has had only limited space at his disposal, and hence only the more important matter could be considered. It is the opinion of the reviewer, however, that a more judicious choice of material could have been made. Important as the thermal and electrical equilibrium between nitrogen, oxygen, and nitric oxide undoubtedly is, it hardly deserves approximately one-quarter of the whole volume. These defects render the work less useful for reference purposes than it might otherwise have been, but it can be recommended with confidence to those for whom it is apparently intended, *viz.*, more advanced students who desire a short summary of the technical methods employed for the fixation of atmospheric nitrogen.

The Silver Bromide Grain of Photographic Emulsions. By A. P. H. TRIVELLI and S. E. SHEPPARD. (Rochester, N.Y., 1921: The Eastman Kodak Company. Pp. 143.)

This monograph is the first of a series on the theory of photography which is to be published by the Eastman Kodak Company.

After dealing in the opening chapters with the influence of ammonia on photographic emulsions, the authors discuss in the second and third chapters the dispersity of silver bromide precipitates and the factors which influence it. Use is made here of recent physico-chemical theories of precipitation and especially of the dispersion theory of von Weimarn. The next two chapters are devoted to crystallisation, catalysis, capillarity, and crystal growth. The remainder of the book is taken up with a very complete study of the silver bromide crystal, first when it is formed by precipitation from silver nitrate and potassium bromide without the presence of a protective colloid, and secondly when it is precipitated, as in a photographic emulsion, in the presence of gelatine. The concluding chapter deals with the examination of crystals of silver bromide and silver iodide in polarised light, and an extensive bibliography is appended.

On reading this book one feels, especially in the earlier chapters, that a clearer and more detailed treatment of some of the more involved points would have enhanced its value. Even so, it should prove of use to other workers. It is profusely illustrated, chiefly with many excellent microphotographs of photographic emulsions. A great deal of original work is described, much of it previously unpublished, and a very extensive account is given of the results of other investigators in the same field. This volume is a valuable addition to our photographic literature.

The Preparation of Synthetic Organic Chemicals at Rochester. By C. E. K. MEES and H. T. CLARKE. (Rochester, N Y.; 1921: The Eastman Kodak Company.)

This reprint of a lecture delivered before the Canadian section of the Society of Chemical Industry is a record of the work undertaken at Rochester, N.Y., during the war to prepare the numerous organic compounds required for research and analytical purposes previously imported from Germany. Copies of the reprint may be had on request to the publishers.

The Manufacture of Sugar from the Cane and Beet. By T. H. P. HERIOT. (London, 1920: Longmans, Green & Co. Pp. 426. Price 24s. net.)

This book, which is one of the monographs on Industrial Chemistry edited by Sir Edward Thorpe, is written by the Lecturer on Sugar Technology at the Royal Technical College, Glasgow. It gives a very clear and comprehensive account of the manufacture of sugar from the cane and beet, and the processes for refining cane and beet sugar. It is well illustrated with both line drawings and half-tone blocks. The book is written from a thoroughly quantitative aspect—the only possible one in successful industrial practice—so that the reader can understand how all the processes are accurately controlled and checked. This quantitative practical aspect is well exemplified in the excellent chapter on Capacity and Efficiency of Mills. The chapter dealing with the Principles of Multiple Effect Evaporation is disappointing. This subject is so closely connected with the development of the sugar industry that one would have expected a much fuller and more scientific treatment. Perhaps the author was limited by considerations of space. In the chapters on crystallisation the author had a good opportunity of dealing with the subject from a physico-chemical standpoint, but he does not take it. However one cannot expect everything from a single author.

The book is written from the point of view of the good process controller and works manager rather than from those of the plant designer and researcher. We can be thankful that it is *not* written from the point of view of the purely laboratory chemist.

The author occasionally gives references to larger treatises and to books dealing with special subjects, but there is no bibliography.

Taken all round, the book is an excellent one and gives a clear account of how sugar is manufactured and refined, and how all the various processes are quantitatively set out and controlled, and their efficiencies determined.

Margarine. By WILLIAM CLAYTON. (London, 1920: Longmans, Green & Co. Pp. 183. Price 14s. net.)

This book belongs to the same series as that just reviewed.

The first sentence of the author's preface reads:—

"In this Monograph, the first of its kind in any language, I have attempted to give a succinct account of the modern processes of manufacture of margarine."

It will thus be seen that a peculiar interest attaches to the present volume. When it is added—by the reviewer—that the author is a well-trained and capable physical chemist, with a practical knowledge of margarine manufacture, it will be obvious that the reader will look forward to something good. In this he will certainly not be disappointed, for the book is really first class.

The author deals with the origin, and the physical and chemical properties of his raw materials (including edible hydrogenated oils), the examination of milk for use in margarine manufacture, the analysis of butter, the processes and apparatus used in margarine manufacture (with numerous illustrations in the form of half-tone plates and figures in the text), nutritional chemistry in its relation to milk, butter, and margarine, and the theory of emulsification.

From his theoretical and practical knowledge, the author shows that margarine manufacture is full of the most interesting problems in physics and physical chemistry. The book contains a very comprehensive bibliography (36 pages), and a patents index, as well as subject and author indexes.

The chapter on emulsification is an excellent account of facts and theories dealing with this subject, and serves to illuminate the chapters dealing with the processes of manufacture. The reviewer has only one complaint to make. Half-tone blocks showing pictures of technical apparatus no doubt serve a useful purpose. But, generally speaking, line drawings are more instructive.

Mr. Clayton is to be heartily congratulated on having produced a work in every way worthy of the high standard set by Sir Edward Thorpe's series.

Mex Fuel Oil. By The Anglo-Mexican Petroleum Company, Limited. Second Edition. (London, 1921 : George Philip & Son, Ltd. Pp. 215. Price 10s. 6d. net.)

The first edition of this brochure on the properties and uses of Mexican fuel oil appeared in 1914. Since that date Mexico has become the second oil-producing country in the world, and the use of oil fuel as a substitute for coal has greatly extended. Although naturally an *ex parte* publication it collects together a great deal of information of great value to the engineer or metallurgist who is able to make use of oil. The printing, paper, and illustrations make it a pleasure to handle the book.

Electric Furnaces in the Iron and Steel Industry. By W. RODENHAUSER and J. SCHOENWA. Third English Edition by C. H. VON BAUER. (New York, 1920 : John Wiley & Sons ; London : Chapman & Hall. Pp. 460. Price 24s. net.)

The last few years have seen a great extension in the use of the electric furnace, particularly as applied to the refining of steel, but there has been no marked technical development in the design or construction of furnaces. This new English edition of a well-known and much appreciated text-book, therefore, does not contain very much matter not included in the second edition already reviewed in these *Transactions*, but it has been brought well up to date, particularly so far as American practice is concerned.

The Greaves-Etchells 3-phase arc-resistance furnace is now described at greater length than previously, and it is noteworthy that the maximum capacity of this furnace, which is a product of Sheffield, has increased from 6 to 15 tons. In America the use of the Snyder furnace has extended and the preheating of the steel scrap before charging it has been found to yield important economies. Among the new furnaces that have appeared in America during the war are the Greene arc furnace, using a steel-bottom electrode and one or more carbon upper electrodes; the Moore 3-phase arc furnace; the Booth-Hall arc furnace, which claims advantages from the use ot a conducting refractory hearth; and the Ludlam 3-phase furnace with 3-upper graphite electrodes in one line and a solid refractory bottom which claims increased efficiency from its exceptionally low roof.

The electric furnace is now an established auxiliary of the steel maker's equipment. Its achievements during the war are beyond dispute, and the fact that over one thousand electric furnaces are probably now in use for melting or refining steel is eloquent evidence of its value.

The Case-Hardening of Steel. By Harry Brearley. (London, 1921: Longmans, Green & Co. Pp. 207. Price 16s. net.)

This is the second edition of a book which first appeared in 1914, which the author has brought entirely up to date in his own inimitable manner, and in which he deals fully with the generally accepted practices of modern case-hardening.

The book is designed for the practical man, but the essential theoretical considerations have been so carefully interwoven that the student, as well as others interested in the metallurgy of steel, will find it of great value.

The general arrangement of the chapters, with the carefully-chosen sub-headings, and the large number of illustrations, considerably enhance its value.

In the opening chapters the author deals mainly with the principles of the case-hardening of steel with relation to the changes in structure and properties, followed by a description of the carburising operations and reagents. Very little new information is given, and the same may be said of the chapter on the methods of testing. A notable inclusion in this edition is a section dealing with automobile steels which should prove of great assistance to those engaged in the production of such material.

Iron and Steel in Sweden. Edited and published under the control of and in co-operation with Jernkontoret by Aktiebolaget Svenska Teknologföreningens Forlag. (Stockholm, 1921. Pp. 183.)

This is an account (in English) of the Swedish iron and steel industry, intended to give necessary information to buyers of its products. It includes, besides a complete list of every brand of iron and steel made in Sweden, together with the names of the makers of each, an interesting description of all the works. The volume is a tribute to the enterprise of the Swedish Iron Masters' Association (Jernkontoret). We wonder how many foreign editions are in contemplation of the corresponding volume relating to the British Iron and Steel industry!

Economic Mineralogy: A Practical Guide to the Study of Useful Minerals. By Thomas Crook, Chief of the Intelligence and Publication Section, Imperial Resources Bureau. (London, 1921: Longmans, Green & Co. Pp. 492. Price 25s. net.)

It is remarkable that while text-books on chemistry are issued with embarrassing rapidity, works upon mineralogy are few and far between.

In addition to this the above work deals with the subject from an entirely new standpoint.

In his preface the author states that his aim has been to meet the needs of those who wish to restrict their attention to the utilitarian side of the subject. With this object in view and realising the necessity for a sound foundation of the scientific elements that underlie the practice, he has introduced what at first appears as a deal of very elementary matter.

In a short note the different aspect of mineralogy when viewed from a scientific or from a utilitarian standpoint is considered and debated. In the first case the attention is usually confined to well-developed specimens and perfect crystal forms, while in the second more importance is attached to the associations of minerals, their modes of occurrence and relation to one another.

The essential part of the work commences with a chapter on crystals and their symmetry and gives a concise but comprehensive review of crystal forms.

In the chapter on the general and physical character of minerals the author shows that he is able to present his very practical knowledge in a manner that will be easily grasped by the student. Commencing with a short glossary of the terms used in dealing with the massive forms of minerals, their value in identification is explained in detail.

When dealing with crystal optics and the use of the polarizing microscope a brief explanation is given of the wave theory of light and the principle of interference. This explanation appears to be too condensed to be of great value and would be of little use to any one unfamiliar with the subject, while to others it is scarcely necessary. Polarisation, refraction, dispersion, and interference are dealt with in more detail, and some good methods for the optical examination of minerals are given.

In dealing with the chemical examination of minerals one is struck with the same sense of hurry that has already been referred to. The old definitions of the atom and the molecule are much as would be found in an elementary treatise on chemistry, while on the next page or so the author is talking about isomorphism, chemical compounds and the composition of minerals.

As soon as he gets into the technical details of chemical examination the author is in his element, and the tests and details that are given will be found to be of the greatest value in practical work. This valuable character of the work is well shown in the chapter on the physical analysis of crushed rocks, and the simple methods that are given for separating mineral mixtures into their several constituents are very good indeed.

A short chapter is devoted to the geology of economic minerals, and then follows what appears to be the most valuable part of the work dealing with the characteristics of ore and gem minerals.

The ore minerals are arranged in alphabetical order of the metals which they contain, and each mineral, with its composition, properties, source, and all known details concerning it are clearly outlined. In most cases, particularly when dealing with gem minerals, the meaning of the name, the crystallographic character, cleavage, hardness, specific gravity are given, and then the optical and chemical properties, occurrence and distribution. This portion of the book is profusely illustrated by half-tone photographic reproductions which are of great value.

A chapter is devoted to miscellaneous economic minerals, arranged in alphabetical order. It is very comprehensive for it includes the minerals employed in building materials as well as the rare earths and the uranium compounds.

From this brief description of a useful book, it is apparent that the author has placed in the hands of the prospector as well as the student a fund of practical information which it would be difficult to gather elsewhere.

A final chapter is given to determination tables where minerals are arranged as metallic and non-metallic groups, order of specific gravity, lustre, colour, etc., and the book concludes with a good index.

Telephonic Transmission. Theoretical and Applied. By J. G. HILL, Engineer, General Post Office. (London, 1920: Longmans, Green & Co. Pp. viii + 398. Price 21s. net.)

The appearance of this book is a welcome sign that not only are the higher branches of the science of telephony being studied by the small and special staff, whose duties include work of this nature, but also that an endeavour is being made to help others to a knowledge of the fundamental methods of dealing with the propagation of telephonic currents.

The late Silvanus Thompson once told the writer that in his opinion, the best places for the teaching of advanced telephony were the German Government school at Hanover and the Italian school at Rome. It is hoped that this book and the others following it, which are being produced by various members of the staff of the Post Office, will be of great value in improving the opportunities of study of this and kindred subjects in this country. A very little learning of some of the difficulties of the subject would have made many of the voluble complainants of the telephone system of this country during the past two years a little less vocal, and would increase the wonder, which every one with some knowledge of the technique of the subject must feel, that not only is it a marvel that commercial telephony is practicable, but that it works at all even as a laboratory experiment.

Like many other branches of electricity the art has generally been far in front of the science. Long distances, multicore cables and congestion in cities have, we imagine, been the most potent causes of the importance of applying all the assistance that mathematical treatment assisted by experimental development can afford. Telephony is a subject peculiarly dependent on mathematical and physical research for its progress and economy. Mr. Hill's book gives some idea of the methods which are essential to such studies.

In the introduction he explains that the use of hyperbolic functions is necessary for simplifying the treatment of the subject, after which there is a chapter dealing with fundamental mathematical principles, on the second page of which we note a confusion between e as being equal to $\left(1 + \frac{1}{x}\right)^x$ when x is infinite, and e^x when x is finite. Chapters II. and III. deal with the direct currents applied to an infinite line with leakance and resistance, and with a finite line and its "equivalent circuit," followed by a chapter on adding resistance in lumps which leads to a consideration of artificial lines. Alternating currents are introduced by a consideration of the physics of human speech, pointing out that 800 cycles per second is about the mean frequency to be considered, the important range being from half to double this value. Later chapters deal with the mathematical representation of the characteristics of lines and the "loading" of circuits with artificial inductance to annul the effect of capacity. An unimportant misprint occurs in the table on page 153. Interesting illustrations of the details of loading coils are given.

That telephonic spirit the "Phantom" circuit is dealt with, and calculations applied to it. Throughout the book the author has been most wise in giving a large number of numerical examples. To any one learning a new and abstruse subject such examples are essential. Later chapters include one on the use of the properties of the "Standard Cable" and one on the important subject of economics as applied to telephone equipment. A chapter on the new revolutionary agent in wire, as in wireless, transmission, the thermionic valve, closes the book, to which appendices on the mathematical development of the more important expressions are added.

The book is one which we believe breaks new ground in this country, and the author is to be congratulated on the successful completion of what must have been a very arduous task. The other books of the series will be awaited with interest.

Untersuchungen über Schwachstromstörungen bei Einphasen-Wechselstrombahnen. Translated into German by FRANZ KUNTZE. (Munich and Berlin, 1920: R. Oldenbourg. Pp. 159.)

This publication is a translation of a report submitted to the directors of the Swedish Government Railways by a committee, appointed for the purpose, mainly in connection with disturbances of telephone and telegraph circuits by the Kiruna-Norwegian frontier single phase railway. It contains a comprehensive description of the Porjus power-station which is of interest as being the northernmost hydro-electric station of any magnitude in the world. The whole installation lies in the arctic zones and its capacity amounts to 50,000 K.W. To neutralise the effect of the low winter temperatures the turbines and generators are sunk 160 feet down in the ground. It may be mentioned as of special interest to members of the Faraday Society that part of the current is used at Porjus for smelting pig-iron and ferro-alloys. The main section of the work describes an undertaking of unique character both as to daring and ingenuity in overcoming extraordinary difficulties. The mensurations refer to static and electro-magnetic disturbances, which are subjected to careful mathematical analysis, and rules are established for their elimination by means of "suction" transformers, etc. As illustrative of the very latest in electrical engineering the book is well worth a careful perusal.

Report on Heat Insulators. By the Engineering Committee of the Food Investigation Board. (London, 1921: H.M. Stationary Office. Pp. 61. Price 3s. net.)

The Food Investigation Board is one of the Committees of the Department of Scientific and Industrial Research, and the present Report, which contains an account of experimental work conducted by Dr. Ezer Griffiths at the National Physical Laboratory for the Engineering Committee, is the fifth of a series being issued by the Board. The purpose of the investigation here described was to fill up the gaps in our knowledge of the laws regulating the transmission of heat through materials used as heat insulators in cold stores and of the physical properties of those materials.

The results obtained bring out the interesting fact that cork, slagwool, charcoal and wood fibres, if of good quality and dry, all have approximately the same thermal conductivity. As this is about twice that of still air, there is a possibility of finding a better cellular material than any of these and such a material—referred to in a supplement—seems to have appeared in the form of rubber expanded by vulcanisation under high gaseous pressure into a highly cellular form. This material has a density so low as 0·059 to 0·12 and its thermal conductivity is only one and a half times that of still air. The possibilities of this material will be awaited with great interest.

Famous Chemists. The Men and their Work. By Sir WILLIAM A. TILDEN, F.R.S. (London, 1921: George Routledge & Sons, Ltd. Pp. 296. With 38 full-page illustrations. Price 12s. 6d. net.)

An attractive method of learning history is through the medium of biography. This interesting book, therefore, written with scholarly care combined with that felicity of style that we have learned to associate with its veteran author, should go far to spread a knowledge of chemical history and through it a love for chemical science among boys and girls and students of all ages, whose imaginations can be stirred by the story of discovery and the conquest of nature. It is not, strictly speaking, a history of chemistry, but one who has read this book will have acquired a better notion of the development of chemical doctrine, from the time of Boyle to that of Ramsay, than can be gained from the perusal of many a more formal and severe history of the science.

The author's plan has been to select twenty-one names, divided into ten groups, from among the most eminent chemists of the past and to give in each case a sketch of his life and a brief account of his contribution—which in all instances has been in a greater or less degree epoch-making—to the structure of chemical science. The guiding principle underlying the selection is the evolution of the atomic theory from the point of view of the chemist, and it is impossible to criticise the choice of so fundamental a basis. To criticise the actual choice of names would perhaps be an easier task; one wonders, for example, why Williamson has been included and Kekulé omitted. But here, as in an anthology, the bias of the one who selects gives a personal touch which we would not care to dispense with. In one or two other instances, notably in the case of Faraday, it is not made very clear in what way the researches described have contributed to the doctrine on which the book is based.

We have noted with some interest that of the twenty-one names selected, no less than eleven are English, four are French, two Italian, two Swedish, one German, and one Russian. Even allowing for a natural bias on the part of the author, the great preponderance of English names is a legitimate source of patriotic gratification.

Contrasted with this an uncomfortable reflection arises in our mind as we close this book. How many young people in this country who have passed through the ordinary elementary and secondary school, and even through the public school, unless on the science side, will be sufficiently equipped to understand it and appreciate it? On the answer to this question must largely depend a just evaluation of our present educational system and we fear greatly that the judgment can be anything but favourable.

The Life and Work of Sir Jagadis C. Bose. By PATRICK GEDDES. (London, 1920: Longmans, Green & Co. Pp. 259. Price 16s. net.)

As a general rule biography of the living subject is to be deprecated. We feel this the more strongly in the case of a man of science whose life-work—as happily in the present instance—is still unfinished and whose achievement it is difficult to appraise at its proper worth before it can be judged in its relationship to the scientific work of which it forms a part. Having said this, we gladly admit that a life of Sir Jagadis Bose can justifiably be admitted as an exception to a very proper rule. In the first place he had to struggle against difficulties and prejudices which in all probability he would not have encountered had he been a European working in a European university, although we hope and believe that the ultimate success of Sir Jagadis Bose and recognition of his work, due to his own splendid courage and persistence, will prevent any such difficulties ever again standing in the way of other pioneers among his compatriots who may be inspired by his example to follow in his footsteps. Apart from such considerations, however, difficulties were inherent in the very nature of the work so well described by Professor Geddes in this volume. Professor Bose began his scientific career as a physicist, and his work on electric waves will be recalled by those acquainted with the early experimental investigations in this subject. Little by little he was led to apply his physical methods and conceptions to the study of plant response and irritability and plant movement and growth, and, perhaps not unnaturally, the botanists looked somewhat askance at this intrusion on the part of a physicist into their special domain. With the intrinsic value of Sir Jagadis Bose's work in botany we are not here concerned, but the fact that he has succeeded in applying physical measurements of the utmost refinement and delicacy to the study of vital phenomena and that this work has opened out possibilities that may have far-reaching consequences—such an achievement is of interest to the genuine student in every branch of science, and it is on these grounds in the main that we welcome the appearance of this picturesque biography, even if we would ourselves have been perhaps a little more cautious in our judgments and a little less exuberant in our eulogies. But much may be forgiven to enthusiasm and charm of manner, and these attractive qualities this book certainly does not lack.

The Centenary Volume of CHARLES GRIFFIN & Co., Ltd., Publishers, 1820-1920.

The celebration of the one-hundredth anniversary of the foundation of this famous publishing firm has been made the occasion for the issue of a memorial volume setting forth an account of what Messrs. Griffin have achieved in the way of the publication of scientific technical books since 1820. The record, of which the firm may be justly proud, is not given in the form of a dry catalogue but embodied in some eight or ten chapters dealing with the various sub-divisions of technology and each written in very readable style by an expert in his subject. Thus Dr. W. Garnett deals with science literature, Professor T. Hudson Beare with engineering, Professor W. Gouland with metallurgical works, Professor H. Louis with mining and geological publications, Professor H. H. Hodgson with chemical technology, and so forth, while the late Lord Moulton contributed a Foreword to the volume. Among the publications of historical interest referred to we note such classics as Rankine's famous "Engineering Manuals," Percy's "Metallurgy," and Faraday's "Chemical History of a Candle," while of modern works may be mentioned the fine series of "Text-books on Physics," by Thomson and Poynting. It will be recalled that this firm published, on behalf of the Faraday, Royal Microscopical and Optical Societies the Report on the General Discussion on "The Microscope: Its Design, Construction and Applications" organised by them in 1920.

We offer Messrs. Griffin our hearty congratulations both on their dignified age and their youthful vigour, and we hope they will long continue to serve with such usefulness the world of science and its applications.

Annuaire pour l'an. Publié par le Bureau des Longitudes. (Paris, 1920: Gauthier-Villars et Cie.)

The general arrangement of the "Annuaire" is substantially unchanged, although some items which have appeared in previous issues are omitted from the present volume: such omissions are indicated by references to the previous volumes.

Corrections have been made in certain of the tables of chemical and physical data, *e.g.* those relating to densities, melting and boiling points, electrical wave-lengths, electrochemical equivalents and constants relating to the critical state. The supplement contains two special articles, one by J. Renaud on the prediction of tidal waves, and one from the pen of Ch. Lallemand on the French law of 1919 relating to the M.T.S. (metre, tonne, seconde) system of units for industrial measurements. This article is well worth perusal by physicists and engineers alike. The terms of the legislation are given *in extenso* and a complete table is included showing the fundamental and derived units for geometrical, mass, time, mechanical, electrical, thermal, and photometric measurements.

The indexing of a work of this nature is in itself a problem, and the three-part index with which the volume is provided greatly increases its utility. A valuable feature for those who were prevented from obtaining this very useful reference book during the period of the war is a section dealing with articles which appeared in the "Annuaire" between 1915 and 1919.

The Year Book of the Scientific and Learned Societies of Great Britain and Ireland. (London, 1921: Charles Griffin & Co., Ltd. Pp. 366. Price 15s. net.)

We offer a cordial welcome to the thirty-eighth issue of this invaluable publication, which contains a record of the work done in science, literature, and art during the year ending June 30, 1921. In addition to the work of the societies, an account is given of the scientific activities of such public institutions as the Imperial Institute, National Physical Laboratory, the Rothamsted Experimental Station, the Meteorological Office (a particularly interesting record) and others of a like character.

We notice that the Biochemical Society and the Association of Economic Biologists have been inadvertently omitted; on the other hand, the newly-formed Newcomen Society has already found a place here.

The Scientists' Reference Book and Diary, 1922. (Jas. Woolley, Sons & Co., Ltd., Manchester. Price 3s. 6d. net.)

This is the twenty-fourth year of issue of this useful pocket-book and diary. Among the tables of constants included are tables of numerical factors used in chemical analysis and other information that the working chemist and physicist likes to have at his fingers' ends. Attention may also be drawn to a section on the chemical composition of foods. Introductory sections deal briefly with modern developments in chemistry and physics, and there is also an excellent little epitome of the chemistry of agriculture among other material we have not space to refer to. The list of scientific societies includes only the chief societies, but even so there are such omissions as the Institution of Electrical Engineers. The Conjoint Board of Scientific Societies and the National Union of Scientific Workers, being of general interest, should be included, although we realise the impossibility of completeness in a work of this kind.

Perhaps it would be better to include, say, all the societies affiliated to the Conjoint Board but give fewer details concerning the separate societies.

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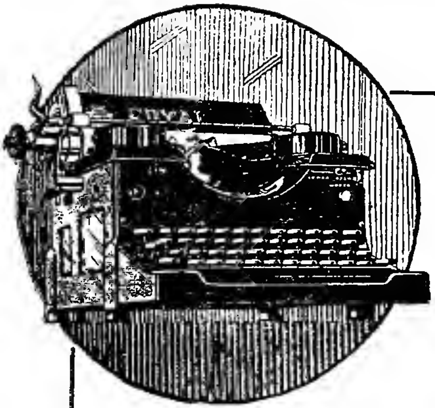

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